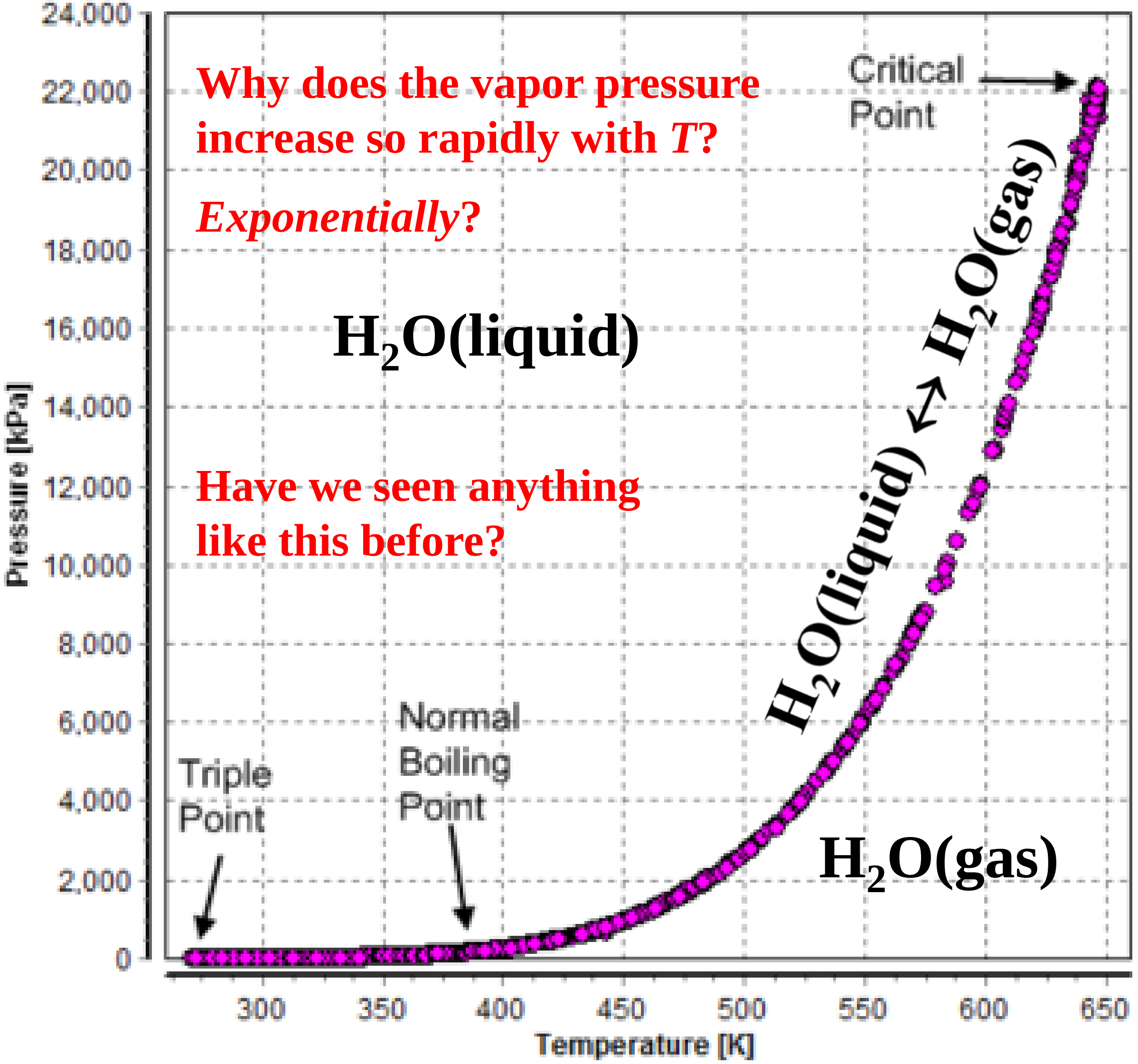
Chapter 8. Phase Diagrams and the Stability of Solids, Liquids and Gases

Summary

- phase diagrams are used to provide graphical representations of conditions required for the existence of solids, liquids or vapors
- the stability of different phases is related to changes in the Gibbs energy with temperature and pressure
- the **phase rule** is introduced to predict the number of different phases that can co-exist at equilibrium
- the effects of **surface tension** at the boundary between phases are introduced

Vapor Pressure Phase Diagram for Water



Why does the vapor pressure increase so rapidly with *T*?

***Exponentially*?**

Have we seen anything like this before?

H_2O(liquid) = H_2O(gas)

Equilibrium constant $K = p_{H2O}$

Data at 25 °C:

$$\begin{aligned}\Delta H^{o} &= \Delta H_{fm}{}^{o}(H_20, g) - \Delta H_{fm}{}^{o}(H_20, l) \\ &= -241{,}818 \text{ J mol}^{-1} - (-285{,}830 \text{ J mol}^{-1}) \\ &= 44{,}012 \text{ J mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G^{o} &= \Delta G_{fm}{}^{o}(H_20, g) - \Delta G_{fm}{}^{o}(H_20, l) \\ &= -228{,}572 \text{ J mol}^{-1} - (-237{,}129 \text{ J mol}^{-1}) \\ &= 8{,}557 \text{ J mol}^{-1}\end{aligned}$$

$$K = \exp(-\Delta G^{o}/RT) = p_{H2O} = 0.0317 \text{ bar}$$

H_2O(liquid) = H_2O(gas)

Temperature Dependence of *K* and p_{H2O} ?

van’t Hoff equation

$$\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = \frac{\mathrm{d}\ln p_{\mathrm{H2O}}}{\mathrm{d}(1/T)} = -\frac{\Delta H^{\mathrm{o}}}{R} \approx \text{constant}$$

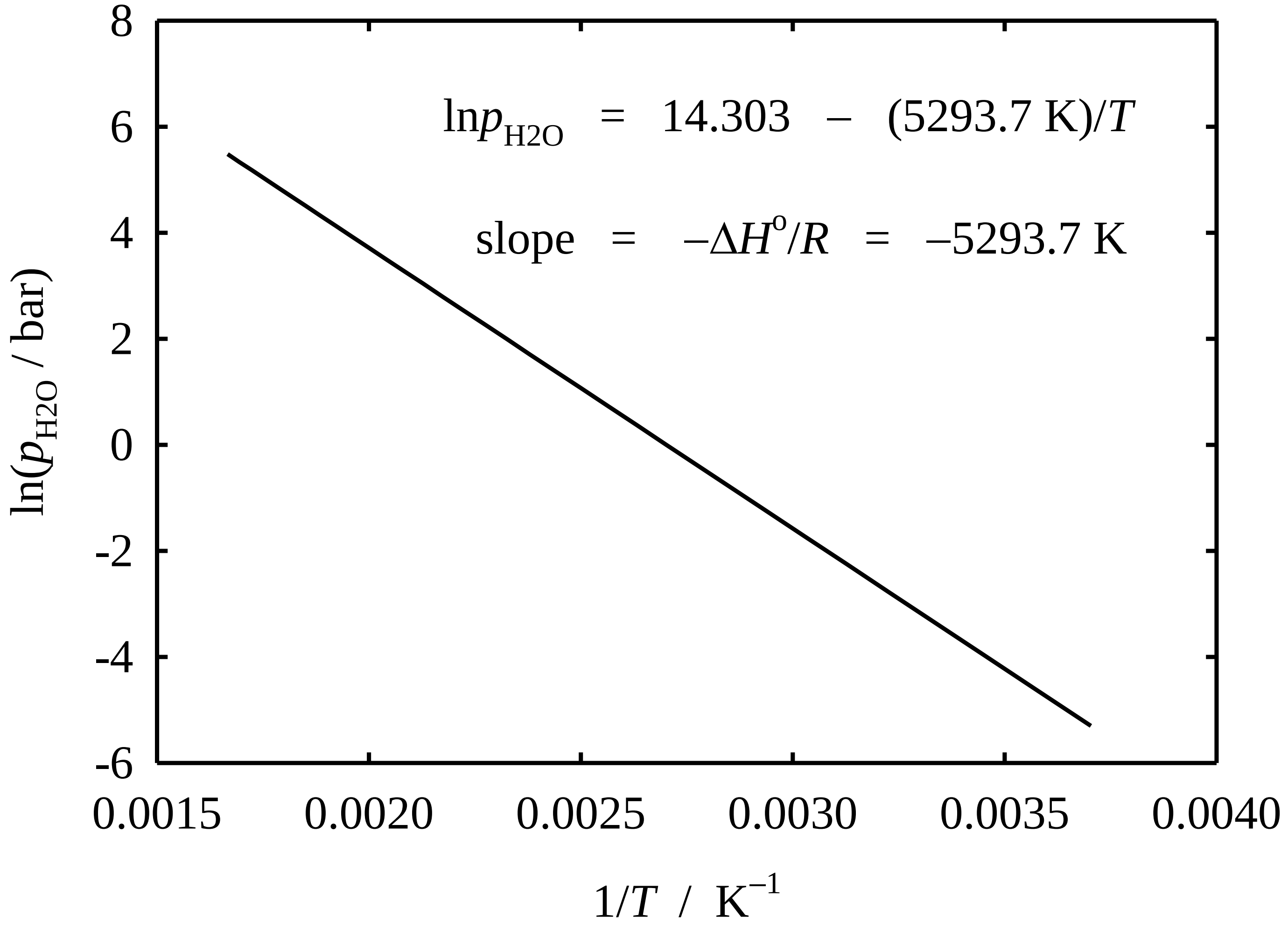
$$\mathrm{d}\ln p_{\mathrm{H2O}} = -\frac{\Delta H^{\mathrm{o}}}{R}\,\mathrm{d}\frac{1}{T}$$

Integrate:

$$\ln p_{\mathrm{H2O}}(T) - \ln p_{\mathrm{H2O}}(298.15\ \mathrm{K}) = -\frac{\Delta H^{\mathrm{o}}}{R}\left(\frac{1}{T} - \frac{1}{298.15\ \mathrm{K}}\right)$$

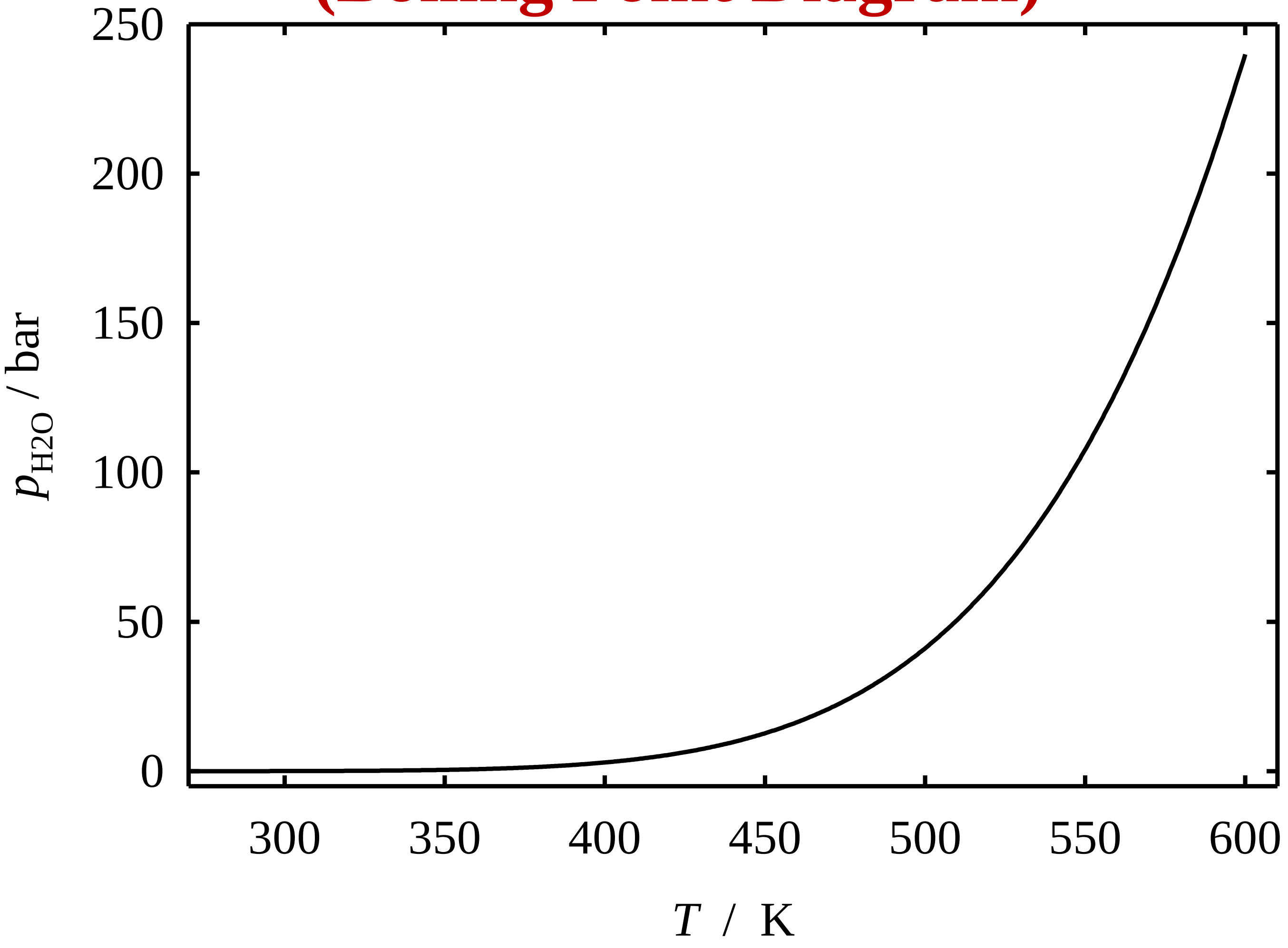
H_2O(liquid) = H_2O(gas)

lnp_{H2O} plotted against 1/*T* (linear)



H_2O(liquid) = H_2O(gas)

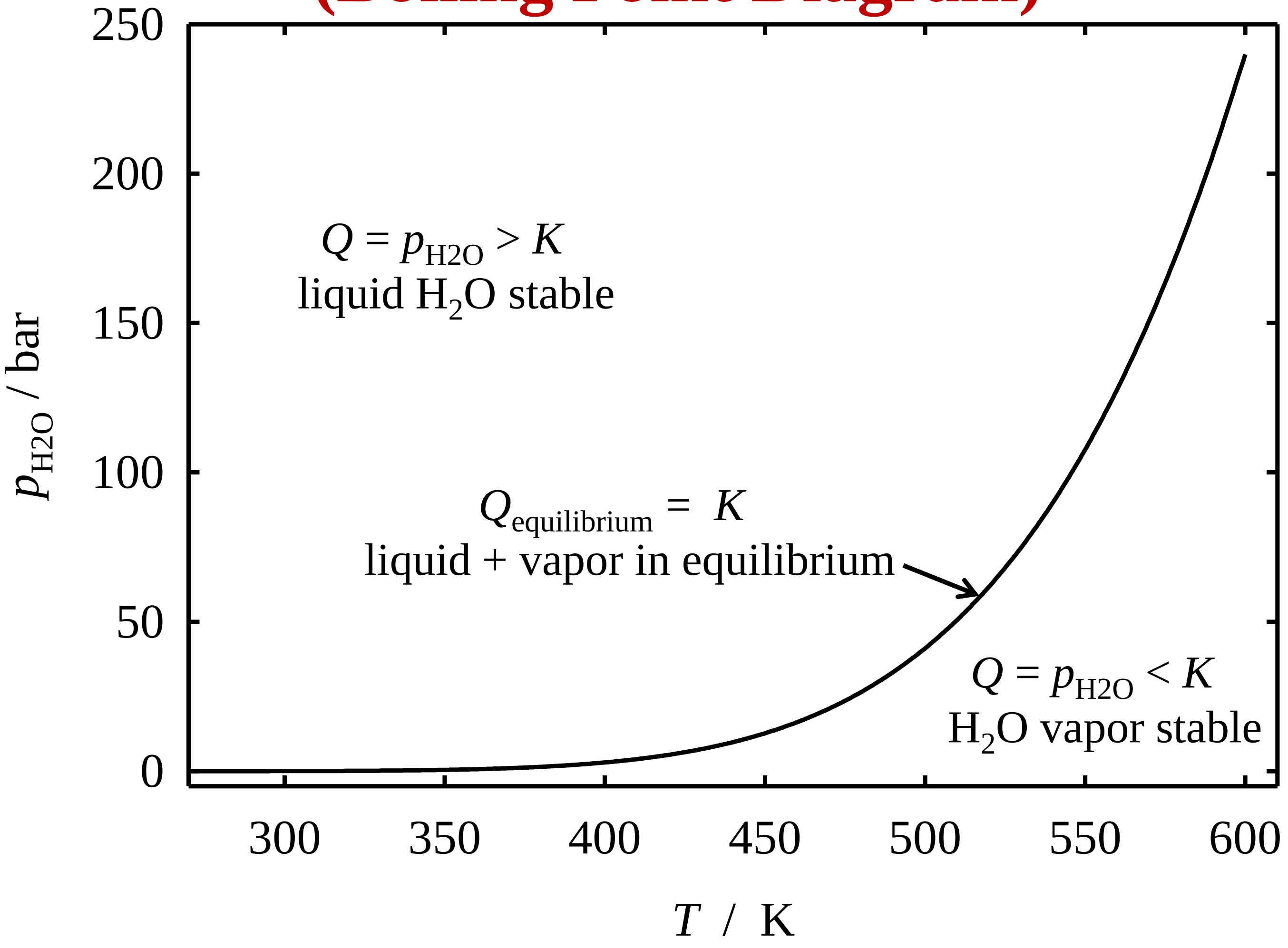
p_{H2O} plotted against T (exponential in 1/T)
(Boiling Point Diagram)



$H_2O(\text{liquid}) \quad = \quad H_2O(\text{gas})$

$K = p_{H2O}$

p_{H2O} plotted against T (exponential in $1/T$)
(Boiling Point Diagram)



$$\mathbf{H_2O(liquid) \quad = \quad H_2O(gas)}$$

$$K = p_{\mathrm{H2O}}$$

This example shows:

<u>phase-diagram regions</u> indicate phases present

<u>phase-diagram lines</u> indicate phases co-existing at equilibrium

<u>phase-diagram lines</u> can provide quantitative thermodynamic data (*e.g.*, enthalpy of vaporization)

Section 8.1 Stability of Solid, Liquid and Gas Phases

What is a "Phase" ?

A form of matter with uniform chemical composition and uniform physical properties (such as density).

example ice (solid water)

Experience suggests:

- solid phases exist at low temperatures
- heating a solid can convert it to a liquid
- heating a liquid converts it to a gas

Relative Stability of Different Phases

How does a **temperature change** affect the stability of a phase?

From $\mathbf{d\mu = dG_m = -S_m dT + V_m dp}$, the change in the chemical potential (Gibbs energy per mole) with temperature is

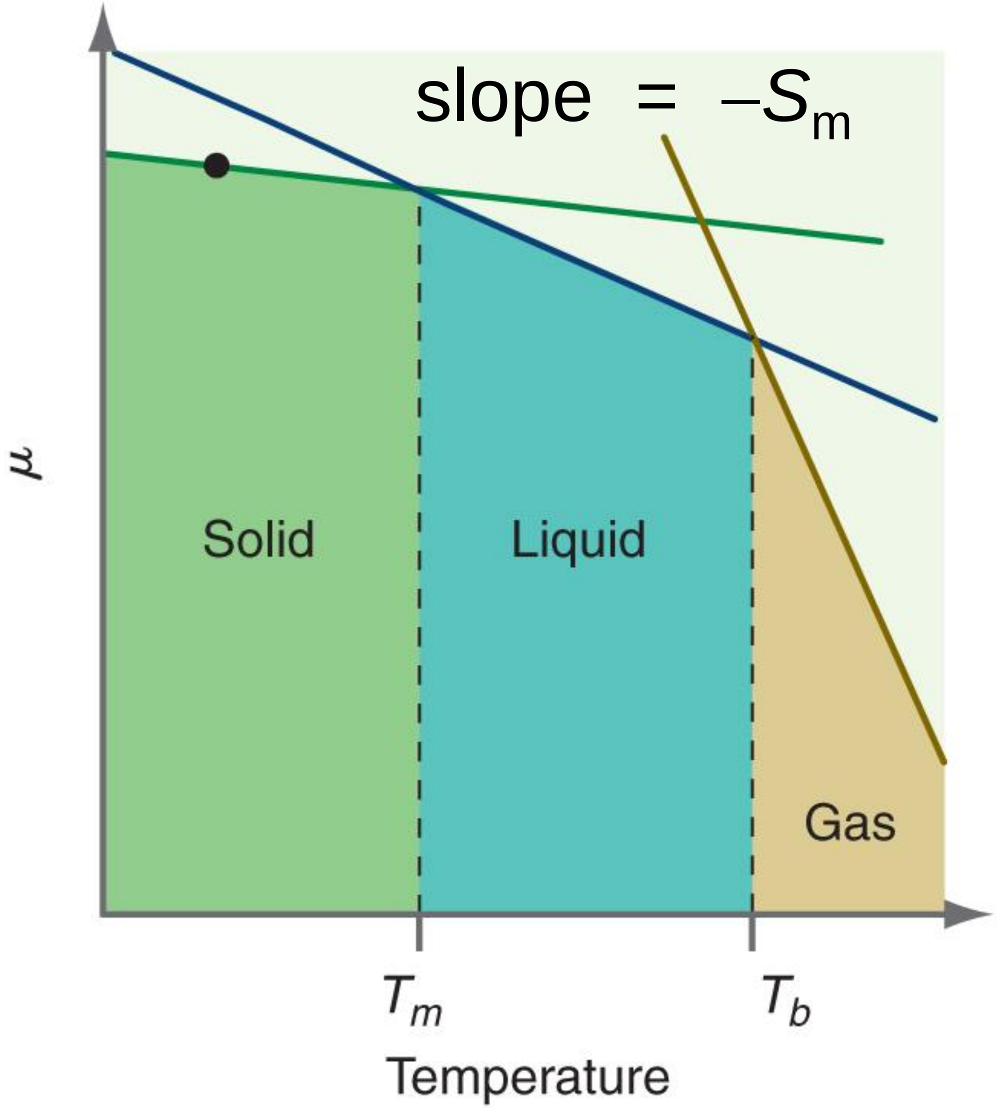
$$\boxed{\left(\frac{\partial \mu}{\partial T}\right)_p = \left(\frac{\partial G_\mathrm{m}}{\partial T}\right)_p = -S_\mathrm{m}}$$

The relative **molar entropies**

$$S_\mathrm{m}(\mathrm{solid}) < S_\mathrm{m}(\mathrm{liquid}) < S_\mathrm{m}(\mathrm{gas})$$

indicate that the chemical potential of the gaseous form of a substance is most sensitive to temperature.

Relative Stability of Different Phases



$T < T_m$ (melting point)
solid most stable
(μ_{solid} lowest)

$T_m < T < T_b$
liquid most stable
(μ_{liquid} lowest)

$T > T_b$ (boiling point)
gas most stable
(μ_{gas} lowest)

Relative Stability of Different Phases

How does a **pressure change** affect the stability of a phase?

From $\mathrm{d}\boldsymbol{\mu} = \mathrm{d}\boldsymbol{G}_\mathrm{m} = -\boldsymbol{S}_\mathrm{m}\mathrm{d}\boldsymbol{T} + \boldsymbol{V}_\mathrm{m}\mathrm{d}\boldsymbol{p}$, the change in the chemical potential (Gibbs energy per mole) with pressure is

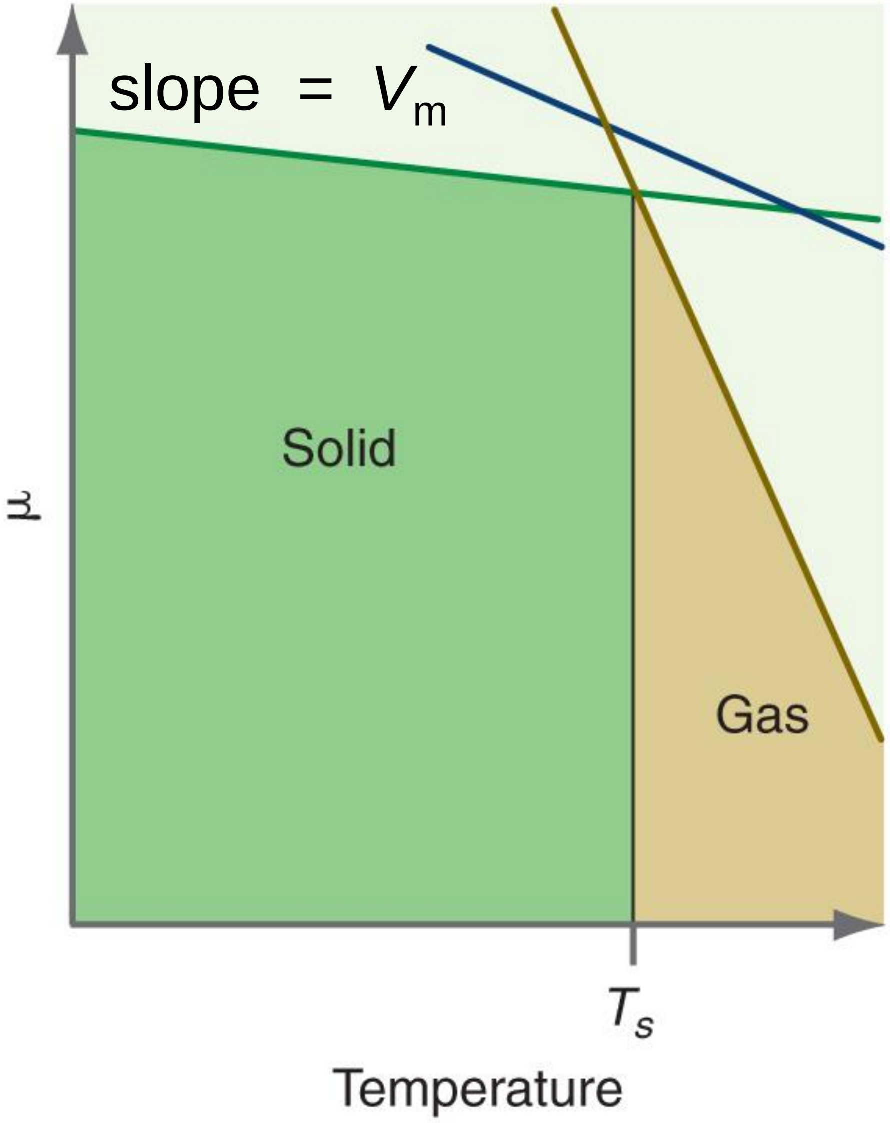
$$\boxed{\left(\frac{\partial \mu}{\partial p}\right)_T = \left(\frac{\partial G_\mathrm{m}}{\partial p}\right)_T = V_\mathrm{m}}$$

The relative **molar volumes**

$V_\mathrm{m}(\text{solid}) \ll V_\mathrm{m}(\text{gas})$ $V_\mathrm{m}(\text{liquid}) \ll V_\mathrm{m}(\text{gas})$

suggests that only the chemical potential of the gaseous form of a substance is appreciably affected by pressure changes.

Relative Stability of Different Phases



At sufficiently low pressures, μ_{gas} can drop below μ_{liquid} allowing direct conversion of **solid to gas** **(**sublimation**)** upon heating.

Application: "Dry" Ice

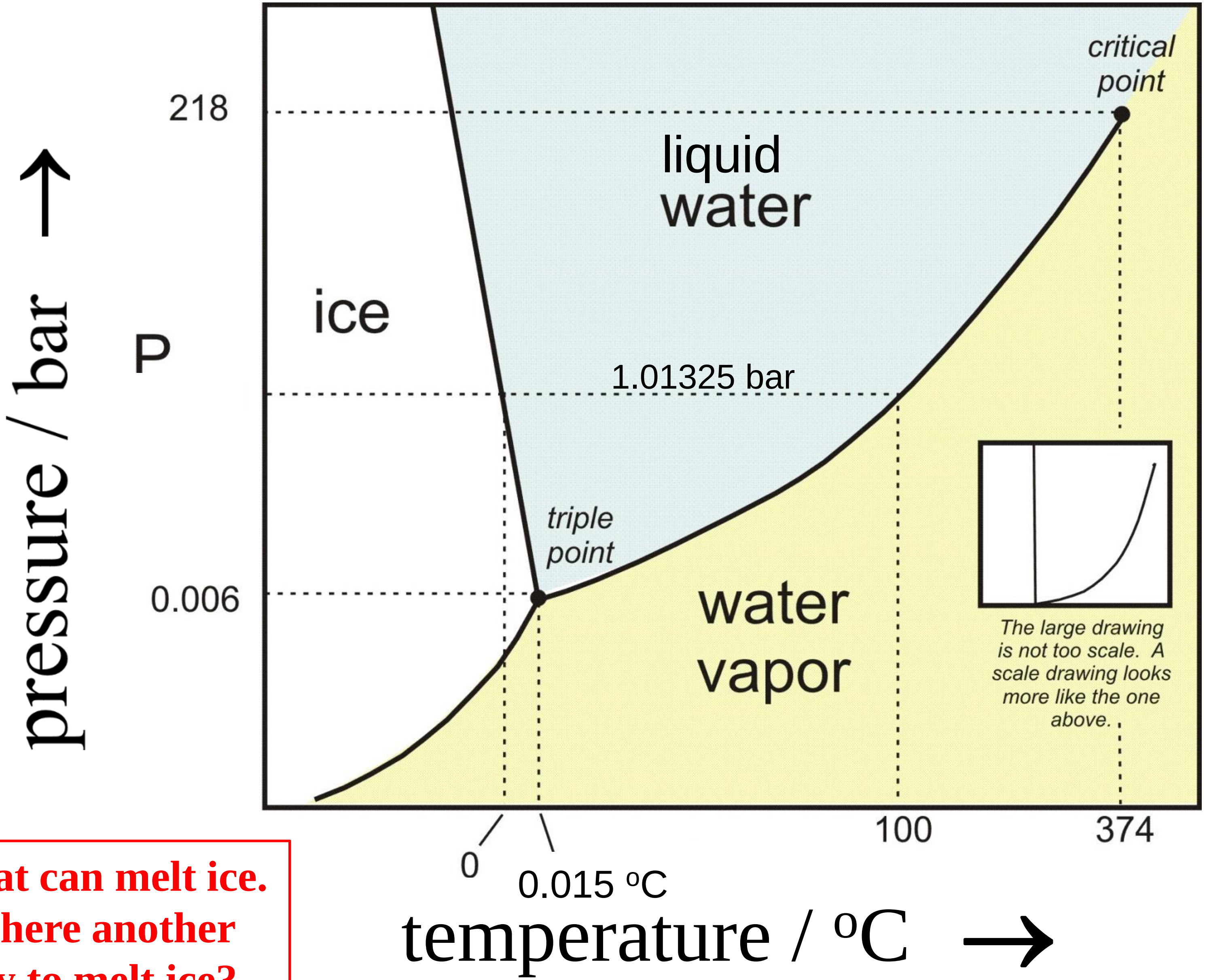
$CO_2(s) \rightarrow CO_2(g)$

A convenient commercial refrigerant that does not form puddles of liquid (like melting ice) that can damage some products.

Section 8.2 Pressure-Temperature Phase Diagrams (for Pure Substances)

- substances can exist as **solids, liquids or gases**
- **what is there** at a given temperature and pressure?
- *p*-*T* phase diagrams provide a convenient **graphical display** of the phase (or phases) present at equilibrium
- *p*-*T* phase diagrams also provide **quantitative information** about enthalpy (and volume) changes for phase transitions
- many **important practical applications**, such as:
  - will we have **rain, snow, dew, or frost ?**
  - **convert graphite to diamond ?**
  - why do **pressure-cookers** work so quickly?
  - why are **high-pressure steam engines** more efficient

Temperature-Pressure Phase Diagram for Water

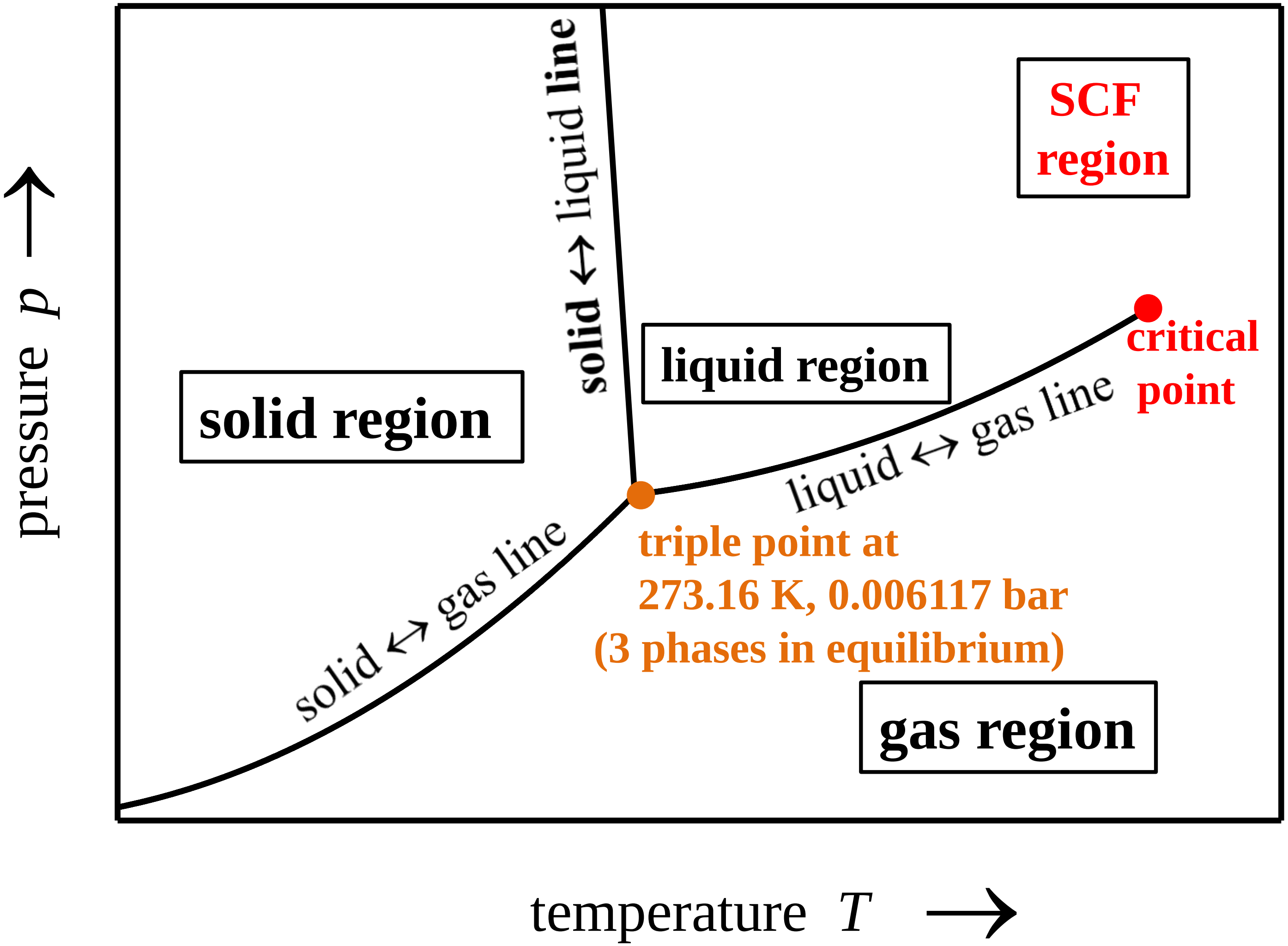


The large drawing is not too scale. A scale drawing looks more like the one above.

- **Heat can melt ice. Is there another way to melt ice?**

Temperature-Pressure Phase Diagram

(pure substance)



critical point

triple point at
273.16 K, 0.006117 bar
(3 phases in equilibrium)

SCF
supercritical fluid
($T > T_c$, $p > p_c$)

Why does the liquid-gas line end at the critical point?

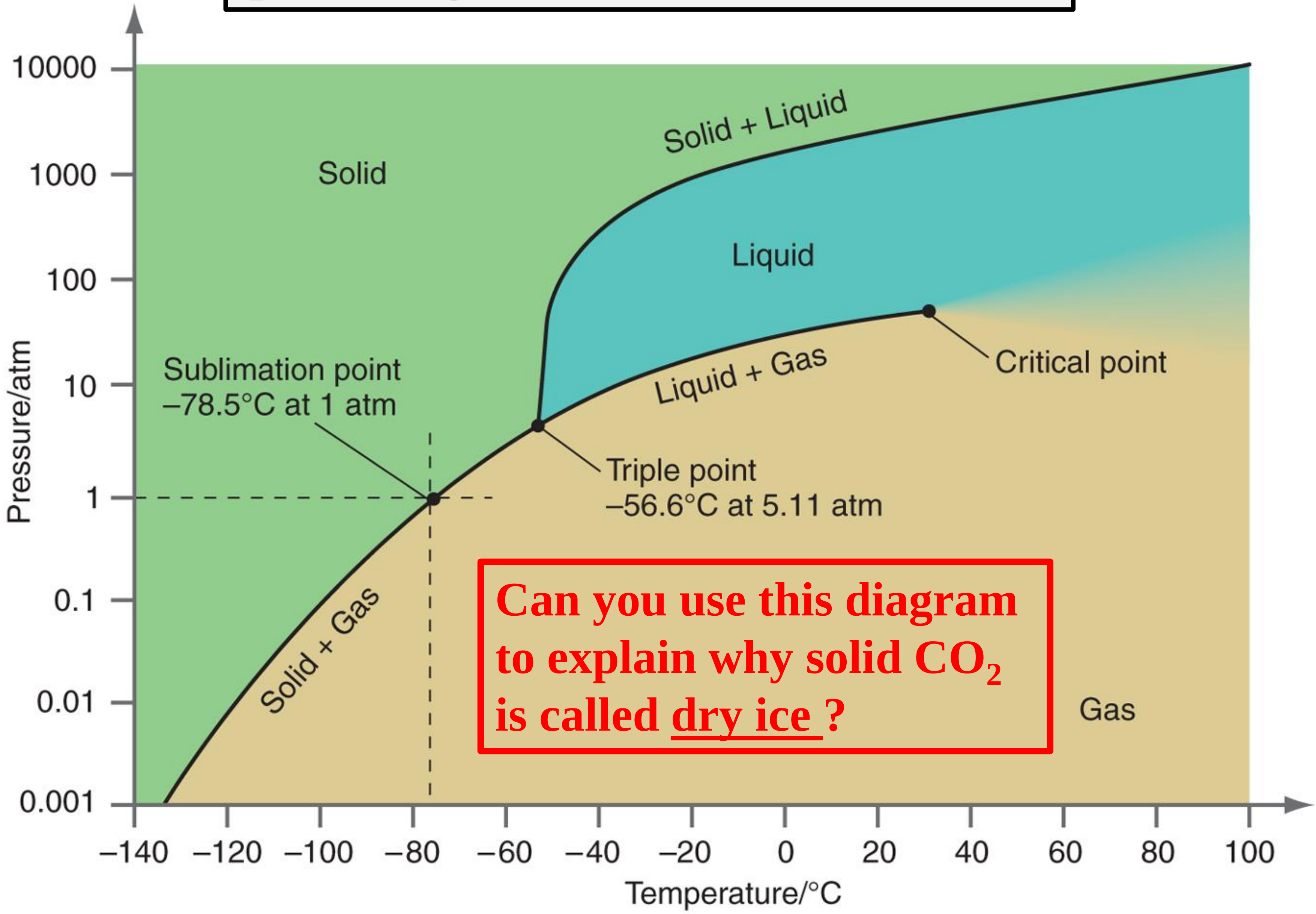
Why is the solid-liquid line so steep?

What is the significance of the triple point?

Critical Points and Gas-Liquid-Solid Triple Points

Substance	T_c / K	p_c / bar	T_{tp} / K	p_{tp} / bar
He	5.25	2.27	2.19	0.051
Ne	44.49	26.79	24.57	0.432
Ar	150.86	48.98	83.81	0.689
Kr	209.35	54.3	115.76	0.741
Xe	289.74	58.4	161.3	0.815
H_2	32.98	12.93	13.84	0.0704
O_2	154.58	50.43	54.36	0.00152
N_2	126.20	33.98	63.18	0.126
CO_2	304.13	73.75	216.55	5.17
CH_4	190.56	45.99	90.68	0.117
CH_3CH_3	305.32	48.72	89.89	8.0×10^{-6}
$CH_3CH_2CH_3$	369.83	42.48	85.47	1.7×10^{-6}
H_2O	647.14	220.64	273.16	0.006117
NH_3	405.40	113.53	195.4	0.06076

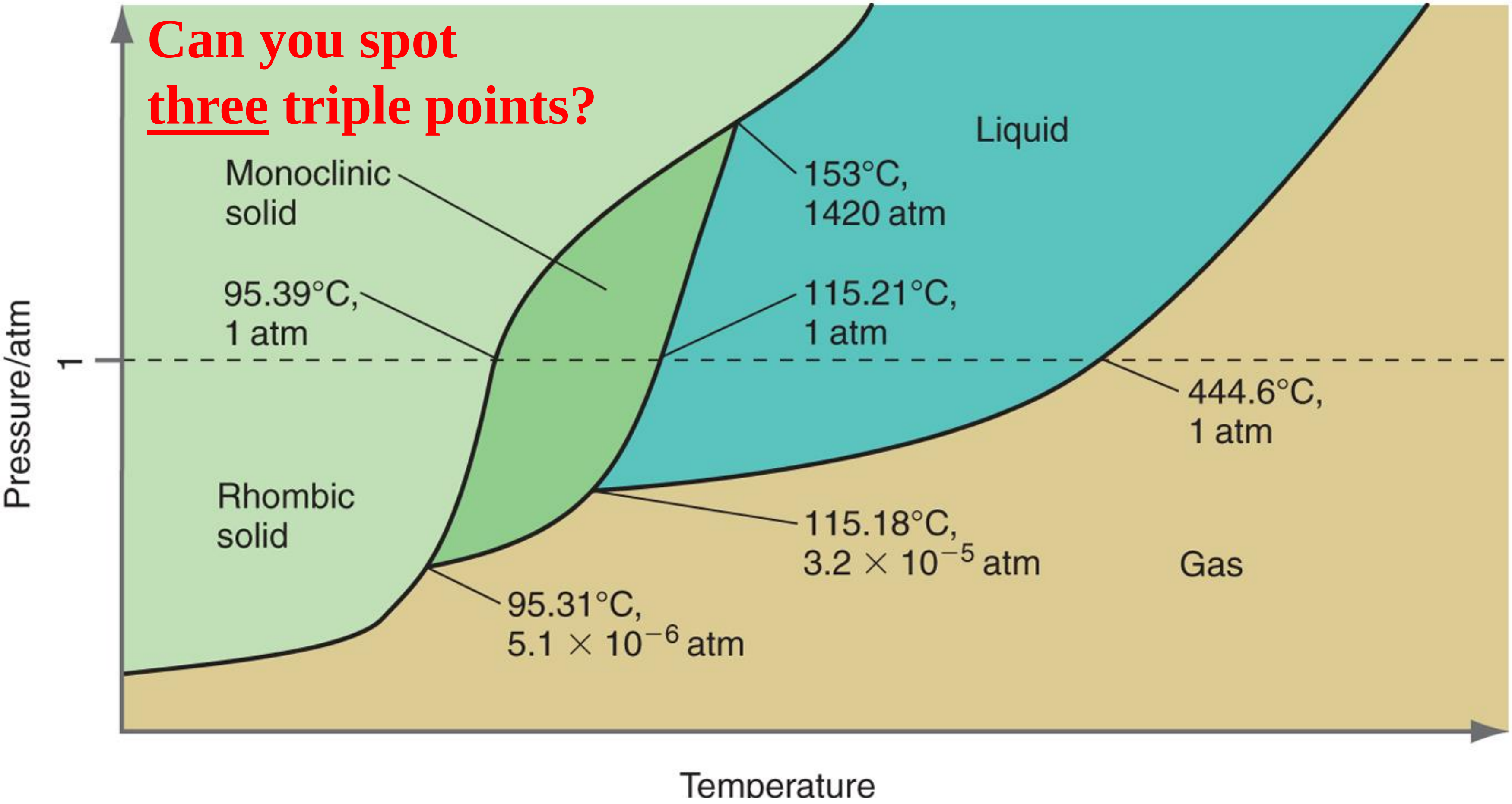
p-*T* Diagram for Carbon Dioxide



Can you use this diagram to explain why solid CO_2 is called dry ice ?

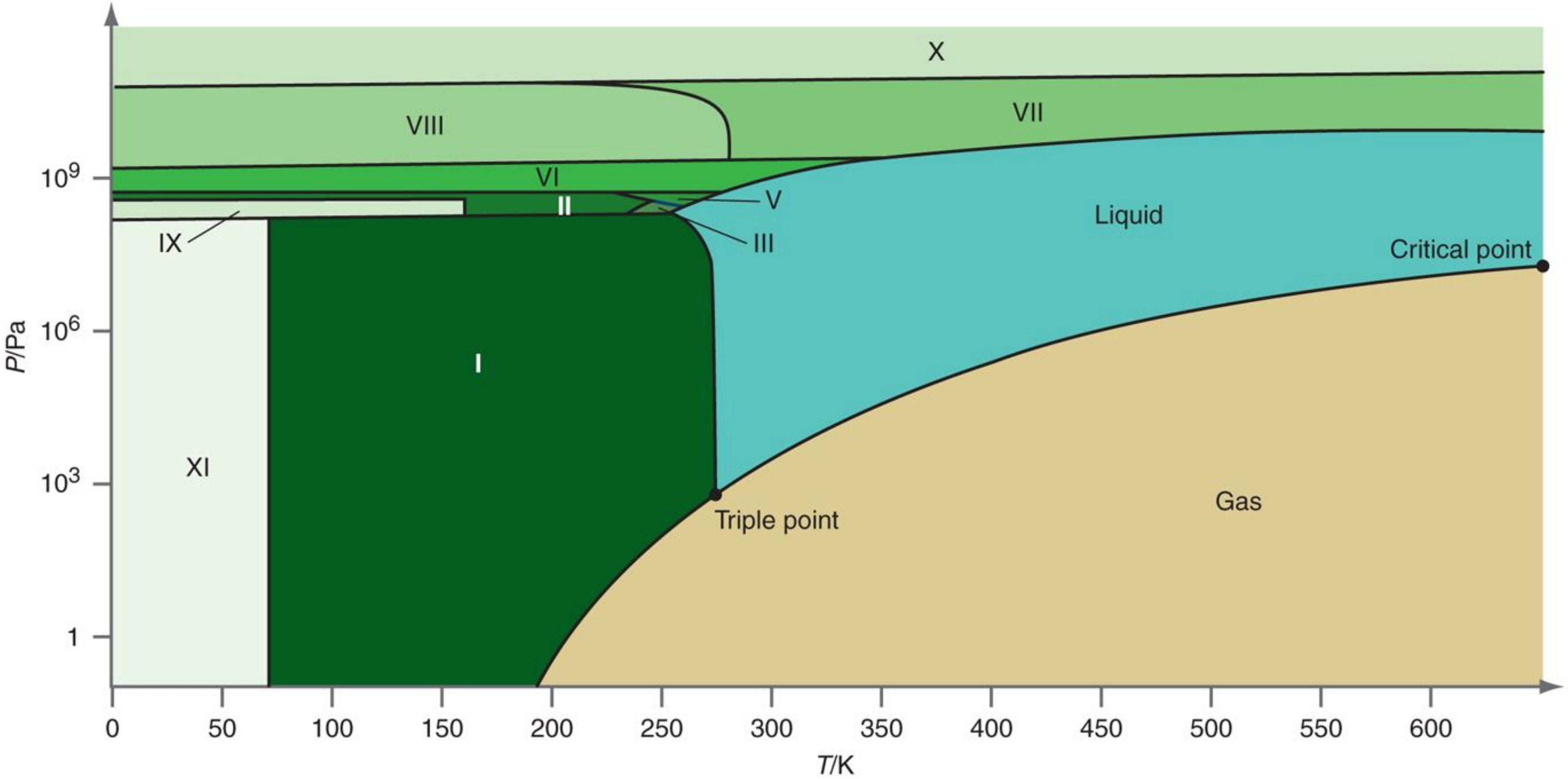
p-*T* Diagram for Sulfur

illustrates the formation of **more than one solid phase**



Can you describe what happens if sulfur is heated from room temperature to 450 ºC at 1 atm?

p-T Diagram for Water up to 10^7 bar



- 11 different forms of crystalline water ("ice") are known
- the "normal" form of ice and snow is Ice I (hexagonal)
- notice that Ice VII has melting temperatures above 200 °C!

Section 8.3 The Phase Rule

Important practical questions:

- how many different phases can co-exist at equilibrium?
- how many independent variables ("degrees of freedom") are needed to specify their states

Pure Substance – One Phase: Two Degrees of Freedom

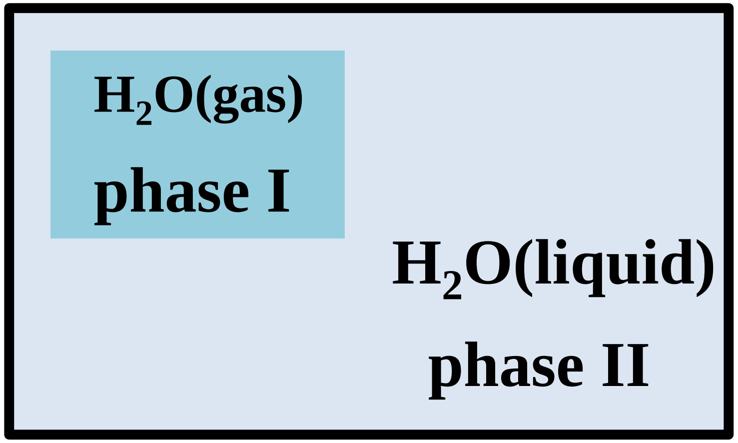
Specifying **two variables**, such as T and p, describes the state of the system and its intensive properties.

Example liquid water at 10 ^{o}C and 2.00 bar.

Example an ideal gas at 300 K and 5.00 bar.
(Note that the molar volume $V_m = RT/p$ variable is not an independent variable at fixed T, p)

Pure Substance – Two Phases: One Degree of Freedom

Two phases (I and II) of a pure substance in equilibrium.



At first glance:

four __independent__ variables?

$T_\mathrm{I} \quad T_\mathrm{II} \quad p_\mathrm{I} \quad p_\mathrm{II}$

Wrong!

thermal equilibrium requires $T_\mathrm{I} = T_\mathrm{II}$
mechanical equilibrium requires $p_\mathrm{I} = p_\mathrm{II}$
chemical equilibrium requires $\mu_\mathrm{I} = \mu_\mathrm{II}$

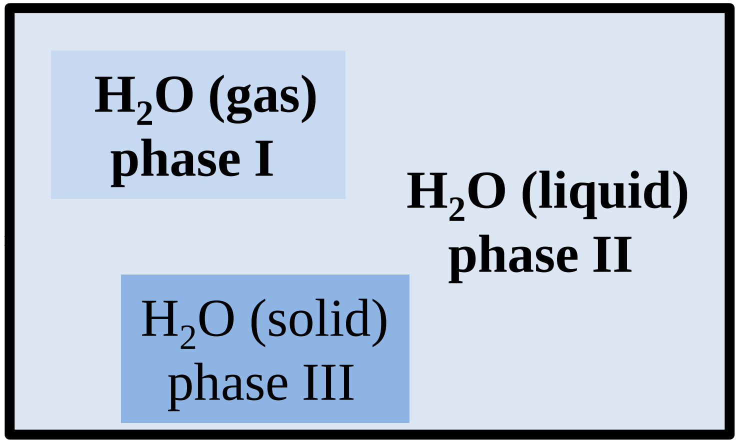
← **3 constraints on 4 variables**

→ only **__one independent variable__**

__Example__ At 100 °C, liquid water and water vapor are in equilibrium only at 1 atm.
p is not an independent variable if *T* is fixed, and *vice versa*.

Pure Substance – Three Phases: ***No Degrees of Freedom***!

Three phases (I, II and III) of a pure substance in equilibrium.



six <u>independent</u> variables?

$T_{\mathrm{I}} \quad T_{\mathrm{II}} \quad T_{\mathrm{III}} \quad p_{\mathrm{I}} \quad p_{\mathrm{II}} \quad p_{\mathrm{III}}$

Wrong *again*!

thermal equilibrium	$T_{\mathrm{I}} = T_{\mathrm{II}}$	$T_{\mathrm{II}} = T_{\mathrm{III}}$
mechanical equilibrium	$p_{\mathrm{I}} = p_{\mathrm{II}}$	$p_{\mathrm{II}} = p_{\mathrm{III}}$
chemical equilibrium	$\mu_{\mathrm{I}} = \mu_{\mathrm{II}}$	$\mu_{\mathrm{II}} = \mu_{\mathrm{III}}$

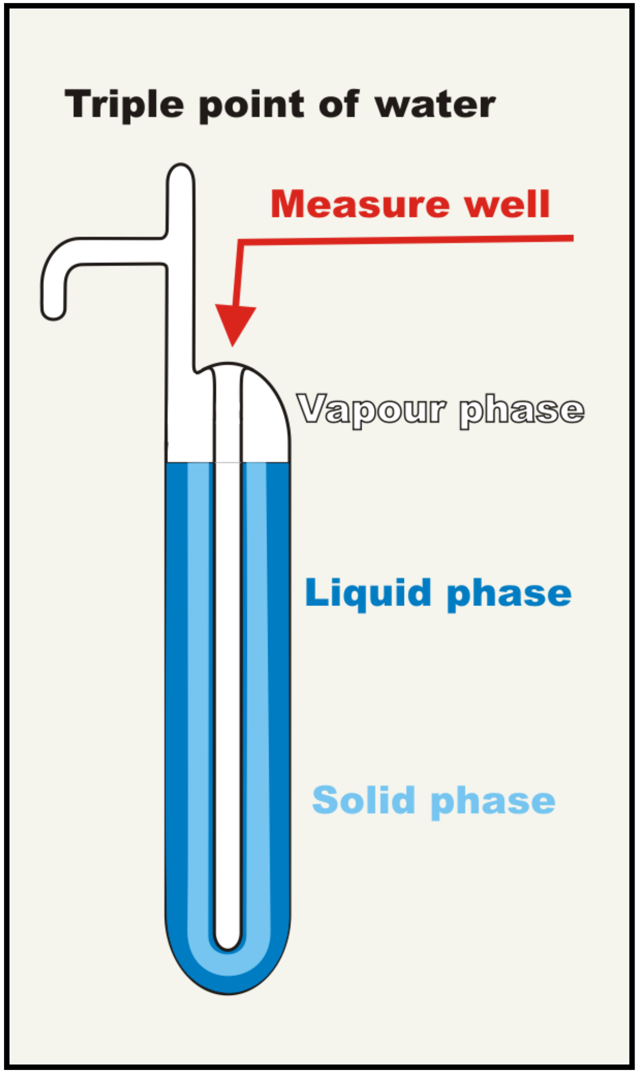
**6 constraints
on
6 variables**

→ **<u>no independent variables (a fixed point)</u>**

<u>Example</u> Water vapor, liquid water, and solid water (ice) are in equilibrium **<u>only at the triple point</u>:** 0.016 °C and 0.006117 bar.

A Practical Application of the Phase Rule

Define the temperature scale and calibrate thermometers



*the **triple point** of water*

(an "invariant" point)

H_2O (vapor)

↙↗ ↖↘

H_2O (solid) ↔ H_2O (liquid)

$$T_{tp} \equiv \mathbf{273.16\ K} \quad (= 0.01\ ^{o}C)$$

defines the temperature scale

using only water, cheap glassware,

and the Phase Rule

Phase Rule

Pure Substances (C = 1 Component)

degrees of freedom = three – number of phases

$$\boxed{F = 3 - P}$$

Systems Consisting of C Components (next Chapter)

$$\boxed{F = C + 2 - P}$$

! Warning !

Phase Rule

! Warning !

Pure Substances ($C = 1$ Component)

$$\boldsymbol{F = 3 - P}$$

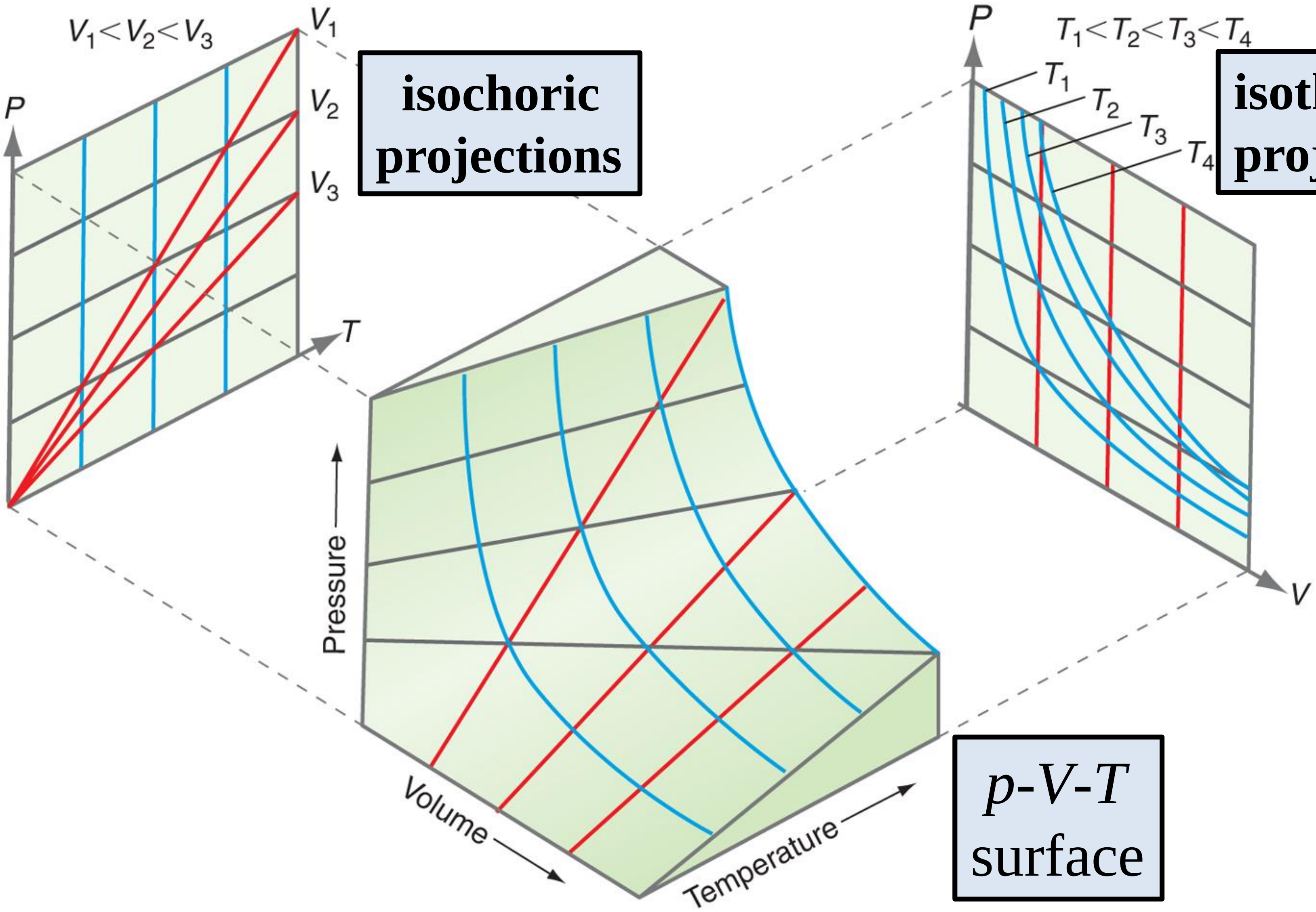
Systems Consisting of *C* Components (next Chapter)

$$\boldsymbol{F = C + 2 - P}$$

These rules apply to equilibrium systems.

Non-equilibrium metastable phases frequently exist, especially for solids (very slow phase conversion **rates**).

Section 8.4 Multidimensional Phase Diagrams

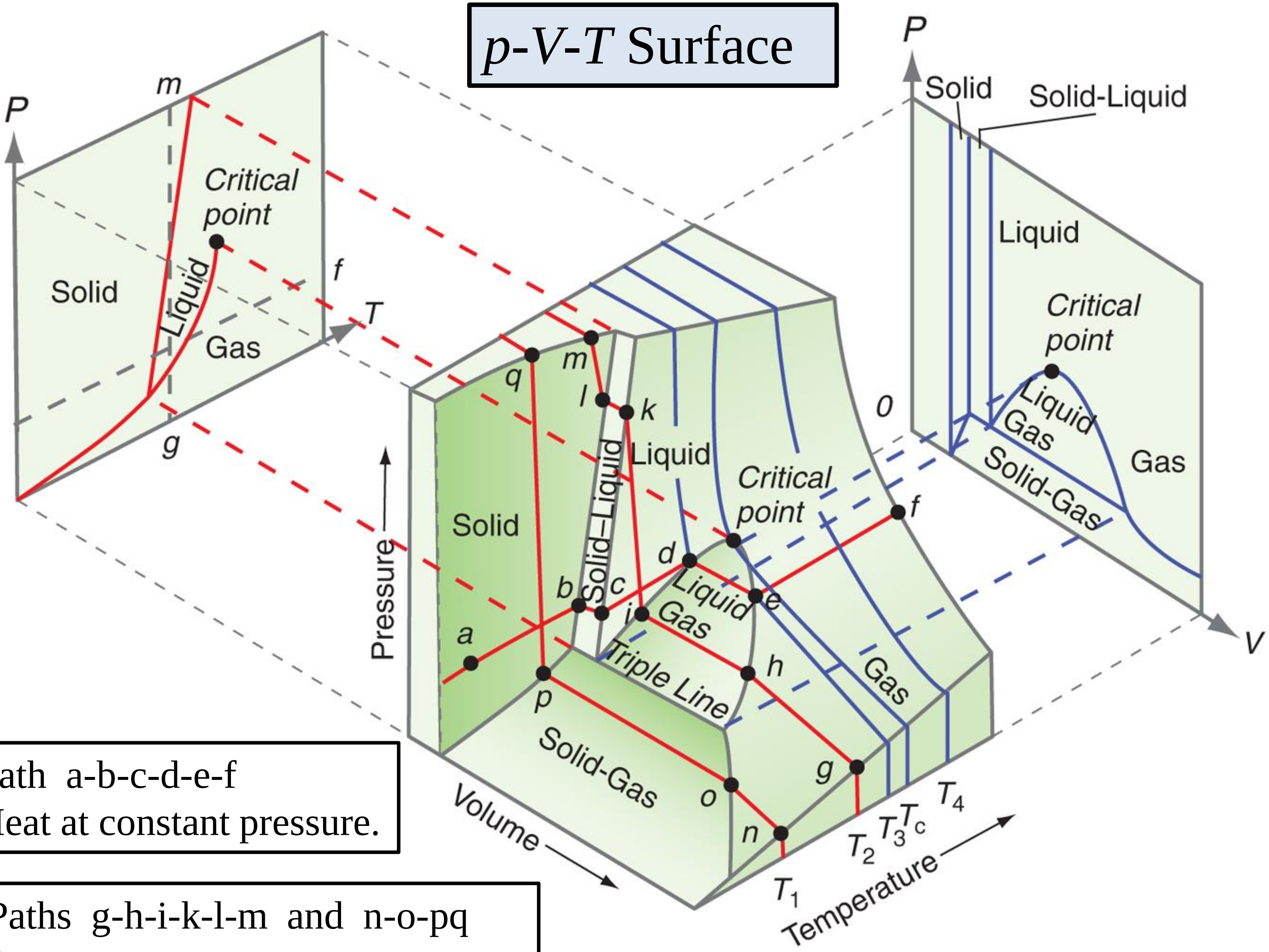


isochoric projections

isothermal projections

p-*V*-*T* surface

p-*V*-*T* Surface



Path a-b-c-d-e-f
Heat at constant pressure.

Paths g-h-i-k-l-m and n-o-pq
Compress at constant temperature.

Sections 8.5 and 8.6 Thermodynamics of Phase Diagrams

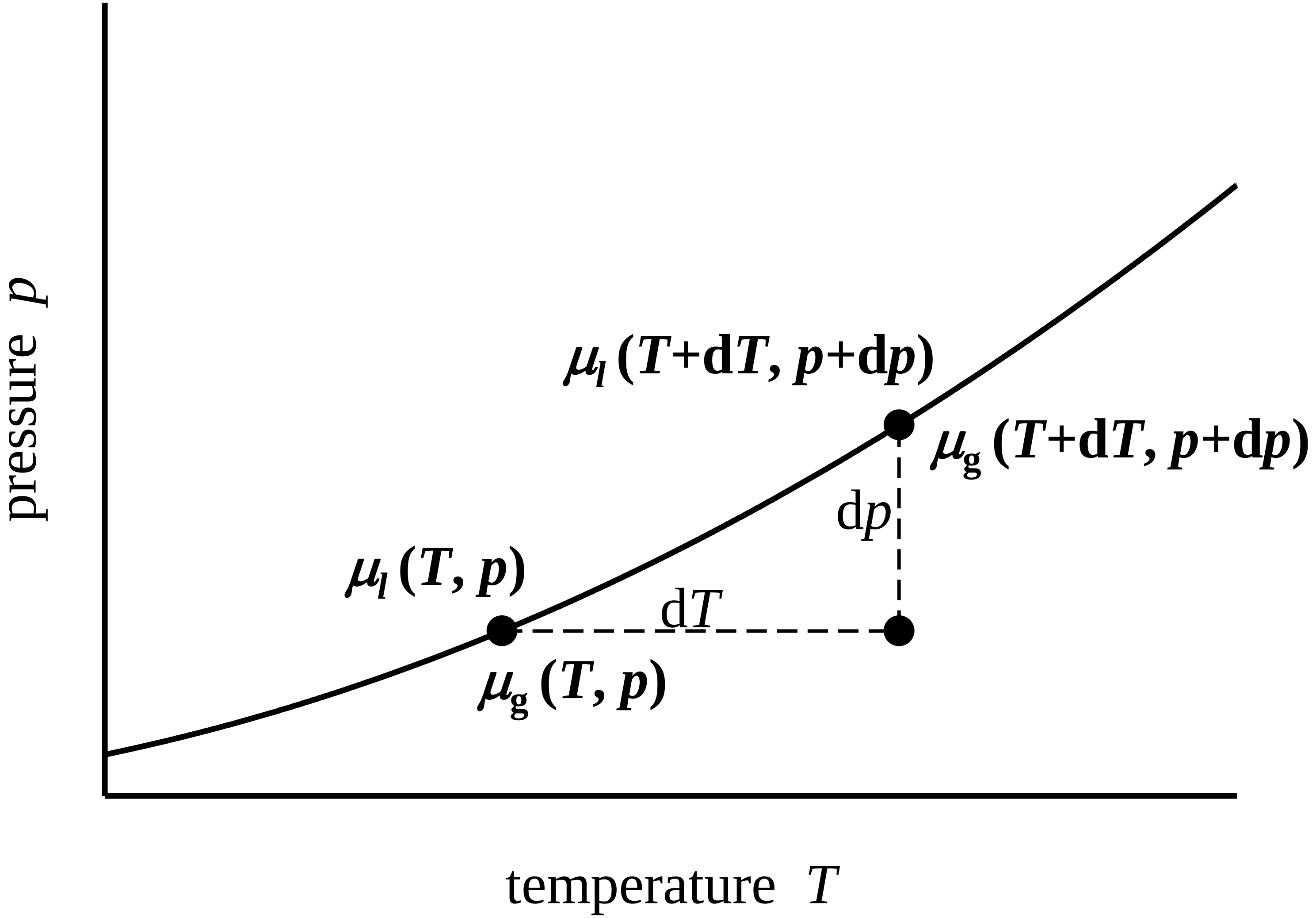
Phase diagrams provide information such as:

- boiling points
- freezing points
- critical points
- co-existence curves for the equilibrium of two phases
- triple points for three phases in equilibrium

Using the 1st and 2nd Laws, enthalpy and entropy changes for phase transitions can also be determined, *without calorimetry*.

Example $H_2O(l) \leftrightarrow H_2O(g)$

The chemical potentials (Gibbs energy per mole) of the liquid and the gas are equal at each point along the boiling curve.



Equilibrium at point p, T on the boiling-point curve:

$$\mu_l(T,p) \;=\; \mu_{\mathrm{g}}(T,p)$$

Equilibrium at neighboring point p + dp, T + dp on the curve:

$$\mu_l(T+\mathrm{d}T,\, p+\mathrm{d}p) \;=\; \mu_{\mathrm{g}}(T+\mathrm{d}T,\, p+\mathrm{d}p)$$

$$\cancel{\mu_l(T,p)} + \left(\frac{\partial \mu_l}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial \mu_l}{\partial p}\right)_T \mathrm{d}p \;=\; \cancel{\mu_g(T,p)} + \left(\frac{\partial \mu_g}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial \mu_g}{\partial p}\right)_T \mathrm{d}p$$

Use $\mathrm{d}G_{\mathrm{m}} = \mathrm{d}\mu = -S_{\mathrm{m}}\mathrm{d}T + V_{\mathrm{m}}\mathrm{d}p$ to get

$$-S_{\mathrm{m}l}\mathrm{d}T + V_{\mathrm{m}l}\mathrm{d}p \;=\; -S_{\mathrm{mg}}\mathrm{d}T + V_{\mathrm{mg}}\mathrm{d}p$$

$$(S_{\mathrm{mg}} - S_{\mathrm{m}l})\mathrm{d}T \;=\; (V_{\mathrm{mg}} - V_{\mathrm{m}l})\mathrm{d}p$$

$$\boxed{\frac{\mathrm{d}p}{\mathrm{d}T} \;=\; \frac{S_{\mathrm{mg}} - S_{\mathrm{m}l}}{V_{\mathrm{mg}} - V_{\mathrm{m}l}} \;=\; \frac{\Delta S_{\mathrm{vap,m}}}{\Delta V_{\mathrm{m,vap}}}}$$

The result for dp/dT for the liquid-gas equilibrium **generalizes to**

Clapeyron Equation

(for ***any*** phase transition)

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S_\mathrm{m}}{\Delta V_\mathrm{m}} = \frac{\Delta H_\mathrm{m}}{T\Delta V_\mathrm{m}}$$

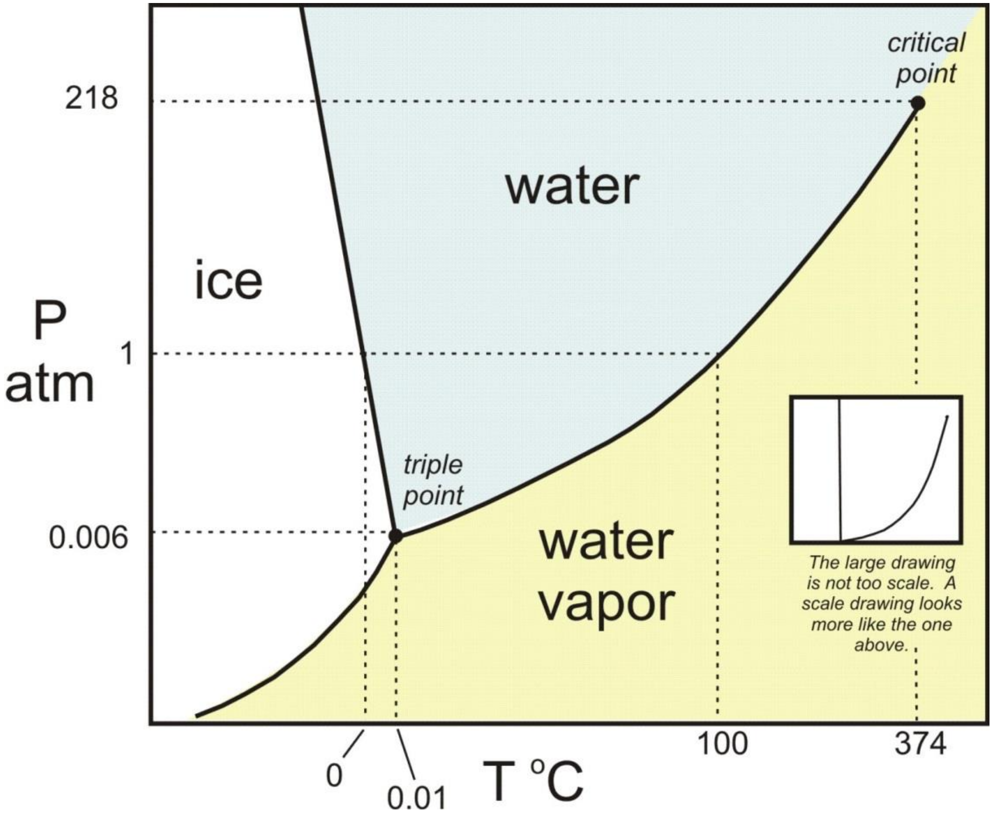
Significance

- ♦ relates phase-diagram slopes to ΔS, ΔH, and ΔV
- ♦ an exact thermodynamic result (no approximations made)
- ♦ applies to liquid-gas, solid-gas, solid-solid transitions
- ♦ valuable source of ΔS and ΔH data – ***without calorimetry***
  (ΔV usually available from density data)

- ● Why can ΔS_m be replaced with $\Delta H_\mathrm{m}/T$?
- ● Why is the ordinary derivative dp/dT used instead of the partial derivative $\partial p/\partial T$?

Example Use the Clapeyron equation to calculate dp/dT for the melting of ice at the triple point.

Why do this? To understand why the melting curve is so steep. Also, why is the slope dp/dT negative, indicating that ice melts at lower temperatures if the pressure is increased.



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Can this help to explain glacier flow and why skating is so fast?

Does high pressure produce a film of liquid water for lubrication?

Example Use the Clapeyron equation to calculate dp/dT for **melting ice** at the triple point.

$$\mathbf{H_2O(s) \leftrightarrow H_2O(\mathit{l})}$$

Data at the water triple point (273.16 K, 0.006117 bar)

$\Delta H_{\text{fus,m}} = 6010\ \text{J mol}^{-1}$

H_2O(s) density = $0.931\ \text{g cm}^{-3} = 931.\ \text{kg m}^{-3}$

$V_{\text{ms}} = (18.01\ \text{g mol}^{-1}) / 0.931\ \text{g cm}^{-3} = 19.34\ \text{cm}^3\ \text{mol}^{-1}$

$H_2O(l)$ density = $1.000\ \text{g cm}^{-3} = 1000.\ \text{kg m}^{-3}$

$V_{\text{m}l} = (18.01\ \text{g mol}^{-1}) / 1.000\ \text{g cm}^{-3} = 18.01\ \text{cm}^3\ \text{mol}^{-1}$

$\Delta V_{\text{m}} = V_{\text{m}l} - V_{\text{ms}} = 18.01 - 19.34 = -1.33\ \text{cm}^3\ \text{mol}^{-1}$

ΔV_{m} explains why dp/dT is negative! (liquid is denser)

$$\frac{dp}{dT} = \frac{\Delta H_{\text{m}}}{T\Delta V_{\text{m}}} = \frac{6010\ \text{J mol}^{-1}}{(273.16\ \text{K})\,(-1.33 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1})} = -1.65 \times 10^{7}\ \ \text{Pa K}^{-1}$$

$$\boxed{\frac{dp}{dT} = -165\ \ \text{bar K}^{-1}}$$

The equilibrium shifts toward ice as the pressure increases, favoring the phase with the smaller volume (higher density).

Example Use the Clapeyron equation to calculate d*p*/d*T* for the **vaporization of water** at the triple point.

$$H_2O(l) \leftrightarrow H_2O(g)$$

Data at the water triple point (273.16 K, 0.006117 bar)

$\Delta H_{\text{vap,m}} = 45{,}050 \text{ J mol}^{-1}$

$V_{\text{mg}} = RT/p = (0.083144 \text{ bar L mol}^{-1} \text{ K}^{-1})(273.16 \text{ K})/(0.006117 \text{ bar})$
$V_{\text{mg}} = 3713 \text{ L mol}^{-1} = 3.713 \times 10^6 \text{ cm}^3 \text{ mol}^{-1}$

$H_2O(l)$ density $= 1.000 \text{ g cm}^{-3} = 1000. \text{ kg m}^{-3}$
$V_{\text{m}l} = (18.01 \text{ g mol}^{-1}) / 1.000 \text{ g cm}^{-3} = 18.01 \text{ cm}^3 \text{ mol}^{-1}$

$\Delta V_{\text{m}} = V_{\text{m}l} - V_{\text{ms}} = 3.713 \times 10^6 - 18.01 = 3.713 \times 10^6 \text{ cm}^3 \text{ mol}^{-1}$

$$\frac{dp}{dT} = \frac{\Delta H_{\text{m}}}{T\Delta V_{\text{m}}} = \frac{45{,}050 \text{ J mol}^{-1}}{(273.16 \text{ K})\,(3.713 \text{ m}^3 \text{ mol}^{-1})} = 44.4 \text{ Pa K}^{-1}$$

$$\boxed{\frac{dp}{dT} = 0.000444 \text{ bar K}^{-1}}$$

d*p*/d*T* for vaporization is much smaller than d*p*/d*T* for melting (–165 bar K^{-1}) because ΔV_{m} for vaporization is so much larger.

Clausius-Clapeyron Equation

For **vaporization** and **sublimation**

liquid → gas $\Delta V_\mathrm{m} = V_\mathrm{mg} - V_{\mathrm{m}l} \approx V_\mathrm{mg}$

solid → gas $\Delta V_\mathrm{m} = V_\mathrm{mg} - V_\mathrm{ms} \approx V_\mathrm{mg}$

Clausius noted $\Delta V_\mathrm{m} \approx RT/p$ and modified the Clapeyron equation:

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_\mathrm{m}}{T\Delta V_\mathrm{m}} \approx \frac{\Delta H_\mathrm{m}}{T(RT/p)}$$

$$\boxed{\frac{\mathrm{d}\ln p}{\mathrm{d}\left(\frac{1}{T}\right)} = -\frac{\Delta H_\mathrm{m}}{R}}$$

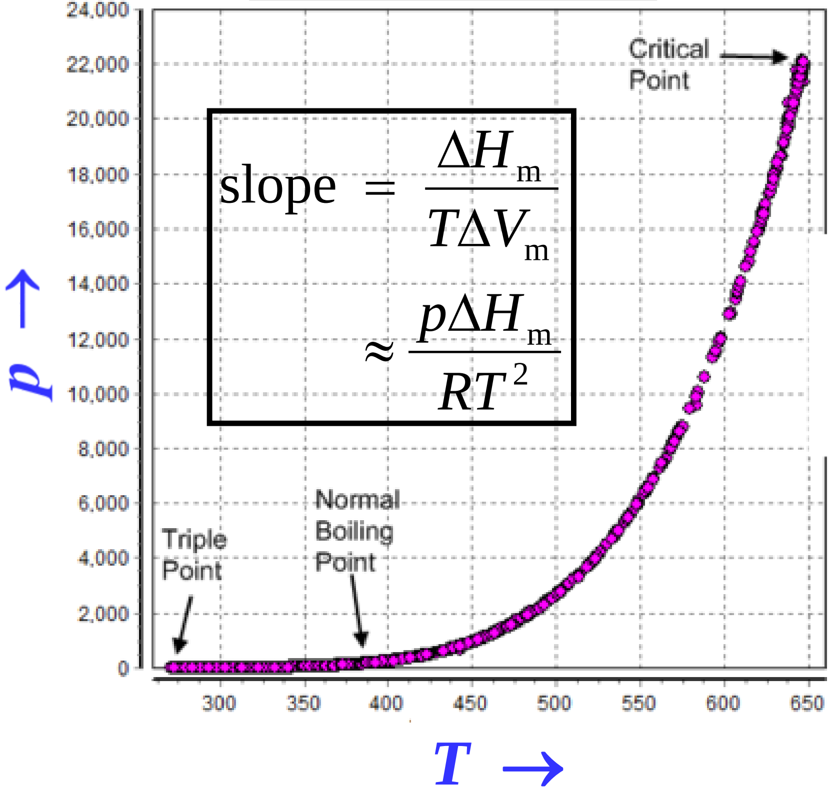
[using $\mathrm{d}(1/T) = T^{-2}\mathrm{d}T$ and $\mathrm{d}\ln p = \mathrm{d}p/p$]

Clapeyron Equation

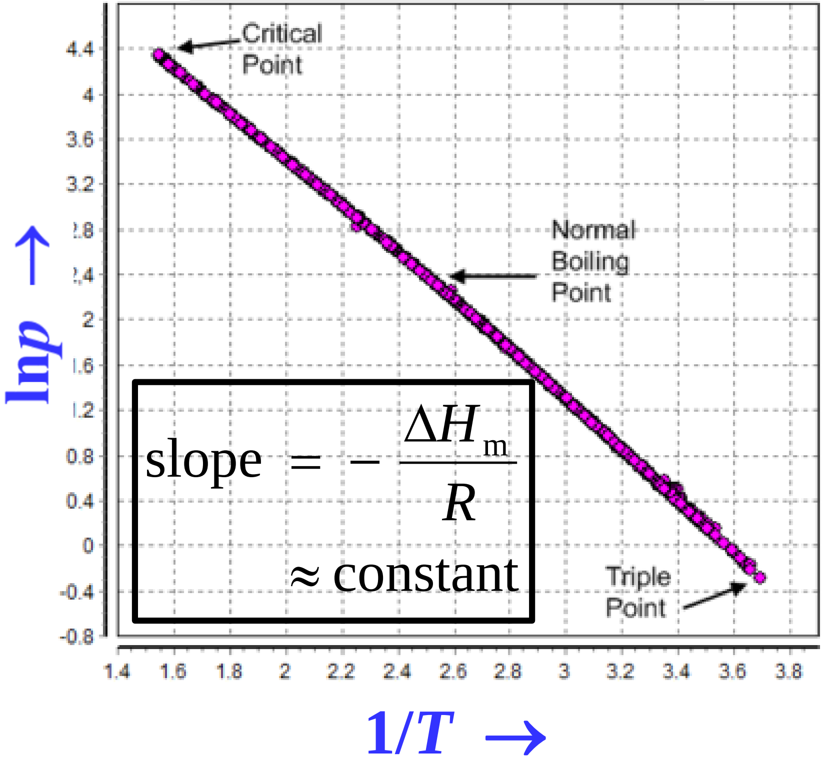
Clausius-Clapeyron Equation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_\mathrm{m}}{T\Delta V_\mathrm{m}}$$

$$\frac{\mathrm{d}\ln p}{\mathrm{d}\left(\frac{1}{T}\right)} = -\frac{\Delta H_\mathrm{m}}{R}$$



$$\text{slope} = \frac{\Delta H_\mathrm{m}}{T\Delta V_\mathrm{m}} \approx \frac{p\Delta H_\mathrm{m}}{RT^2}$$



$$\text{slope} = -\frac{\Delta H_\mathrm{m}}{R} \approx \text{constant}$$

Clausius-Clapeyron Equation

For **vaporization** **and** **sublimation**, assuming $\Delta V_\mathrm{m} = RT/p$:

$$\mathrm{d}\ln p = -\frac{\Delta H_\mathrm{m}}{R}\,\mathrm{d}\frac{1}{T}$$

Integrate assuming constant ΔH_m

$$\int_{\ln p_1}^{\ln p_2} \mathrm{d}\ln p = -\int_{1/T_1}^{1/T_2} \frac{\Delta H_\mathrm{m}}{R}\,\mathrm{d}\frac{1}{T} \approx -\frac{\Delta H_\mathrm{m}}{R}\int_{1/T_1}^{1/T_2} \mathrm{d}\frac{1}{T}$$

$$\boxed{\ln p_2 \approx \ln p_1 - \frac{\Delta H_\mathrm{m}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

Used to estimate vapor and sublimation pressures at different temperatures

Clausius-Clapeyron Equation

Example The normal boiling point of water (p = 1 atm) is 100 ^{o}C. At this temperature the enthalpy of vaporization is 40,657 J mol^{-1}. Estimate the vapor pressure of water at the triple point temperature (0.01 ^{o}C).

T_1 = 373.15 K p_1 = 1 atm =1.01325 bar

T_2 = 273.16 K p_2 = ?

$$\ln p_2 \approx \ln p_1 - \frac{\Delta H_{\mathrm{vap,m}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln p_2 \approx \ln(1.01325) - \frac{40{,}657}{8.314}\left(\frac{1}{273.16} - \frac{1}{373.15}\right)$$

Calculate p_2 = 0.00836 bar at 0.01 ^{o}C. (Measure 0.00612 bar)

Clausius-Clapeyron Equation

The **Clausius-Clapeyron equation** for the temperature dependence of vapor pressures [A(*l*) → A(g)] and sublimation pressures [A(s) → A(g)]

$$\boxed{\frac{\mathrm{d}\ln p}{\mathrm{d}(1/T)} = -\frac{\Delta H_{\mathrm{m}}}{R}}$$

closely resembles the **van’t Hoff equation** for the temperature dependence of the equilibrium constants of chemical reactions

$$\boxed{\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = -\frac{\Delta H_{\mathrm{R}}^{\mathrm{o}}}{R}}$$

This is no accident! The “equilibrium constant” for A(s) → A(g) and A(*l*) → A(g) is $p_{\mathrm{A}}/p^{\mathrm{o}}$.

Section 8.7 Pressure-Dependence of the Vapor Pressure of Solids and Liquids (Almost Negligible)

The vapor pressure p of a pure liquid at standard pressure p^{o} is calculated from the equilibrium condition

$$\mathrm{A}(\text{liquid}, p^{\mathrm{o}}) \leftrightarrow \mathrm{A}(\text{gas}, p)$$

$$\mu_l^{\mathrm{o}}(p^{\mathrm{o}}) = \mu_{\mathrm{g}}^{\mathrm{o}}(p^{\mathrm{o}}) + RT\,\ln(p/p^{\mathrm{o}})$$

If the liquid is under an applied pressure of $p^{\mathrm{o}} + \Delta p$, the equilibrium is shifted and the vapor pressure of the liquid changes to p^*:

$$\mu_l\,(p^{\mathrm{o}} + \Delta p) = \mu_{\mathrm{g}}^{\mathrm{o}}(p^{\mathrm{o}}) + RT\,\ln(p^*/p^{\mathrm{o}})$$

Using

$$\mu_l(p^\mathrm{o}+\Delta p) \;=\; \mu_l^\mathrm{o}(p^\mathrm{o}) \;+\; \int_{p^\mathrm{o}}^{p^\mathrm{o}+\Delta p} \left(\frac{\partial \mu_l}{\partial p}\right)_\mathrm{T} \mathrm{d}p$$

$$= \mu_l^\mathrm{o}(p^\mathrm{o}) \;+\; \int_{p^\mathrm{o}}^{p^\mathrm{o}+\Delta p} V_{\mathrm{m}l}\,\mathrm{d}p \;\approx\; \mu_l^\mathrm{o}(p^\mathrm{o}) \;+\; V_{\mathrm{m}l}\Delta p$$

shows

$$\mu_l(p^\mathrm{o}+\Delta p) \;=\; \boldsymbol{\mu_l^\mathrm{o}(p^\mathrm{o})} \;+\; V_{\mathrm{m}l}\Delta p$$

$$= \boldsymbol{\mu_\mathrm{g}^\mathrm{o}(p^\mathrm{o}) \;+\; RT\ln(p/p^\mathrm{o})} \;+\; V_{\mathrm{m}l}\Delta p$$

$$= \mu_\mathrm{g}^\mathrm{o}(p^\mathrm{o}) \;+\; RT\ln(p^*/p^\mathrm{o})$$

Find $RT\ln(p^*/p) \;=\; V_{\mathrm{m}l}\Delta p$

pressure increase Δp increases the chemical potential of liquid water by $V_{\mathrm{m}l}\Delta p$

$$\boxed{\frac{\text{vapor pressure of liquid at } p^\mathrm{o}+\Delta p}{\text{vapor pressure of liquid at } p^\mathrm{o}} \;=\; \mathrm{e}^{V_{\mathrm{m}l}\Delta p/RT}}$$

Pressure-Dependence of the Vapor Pressure of Solids and Liquids (Almost Negligible)

Example The vapor pressure *p* liquid water at 25 $^{\mathrm{o}}$C under a a pressure of 1 bar is 3.17 kPa. Calculate the vapor pressure of water at 25 $^{\mathrm{o}}$C under a total applied pressure of 5 bar.

Data: Use 18 $\mathrm{cm^3\ mol^{-1}}$ for the molar volume of the liquid.

$$V_{\mathrm{m}l} = 18 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}}$$

all SI units

$$\Delta p = (5 - 1)\ \mathrm{bar} = 4\ \mathrm{bar} = 400{,}000\ \mathrm{Pa}$$

$$V_{\mathrm{m}l}\Delta p/RT = (18 \times 10^{-6})(400{,}000)/(8.314)(298.15) = 0.00290$$

The vapor pressure increases by about 0.29 % (small effect) to (3.17 bar)$e^{0.00290}$ = 3.179 bar

Section 8.8 Surface Tension

- the thermodynamic properties of gases, liquids and solids are well understood
- what about the properties of the boundaries between these phases?
- interfacial properties can be important for systems with large specific surface areas (surface area per unit mass), such as:
  - bubbles and foams
  - fogs, mists, smokes and suspensions
  - dust, powders and nanoparticles
  - porous materials
  - microemulsions and detergent micelles
  - heterogenous catalysts

Surface Tension - *Applications*

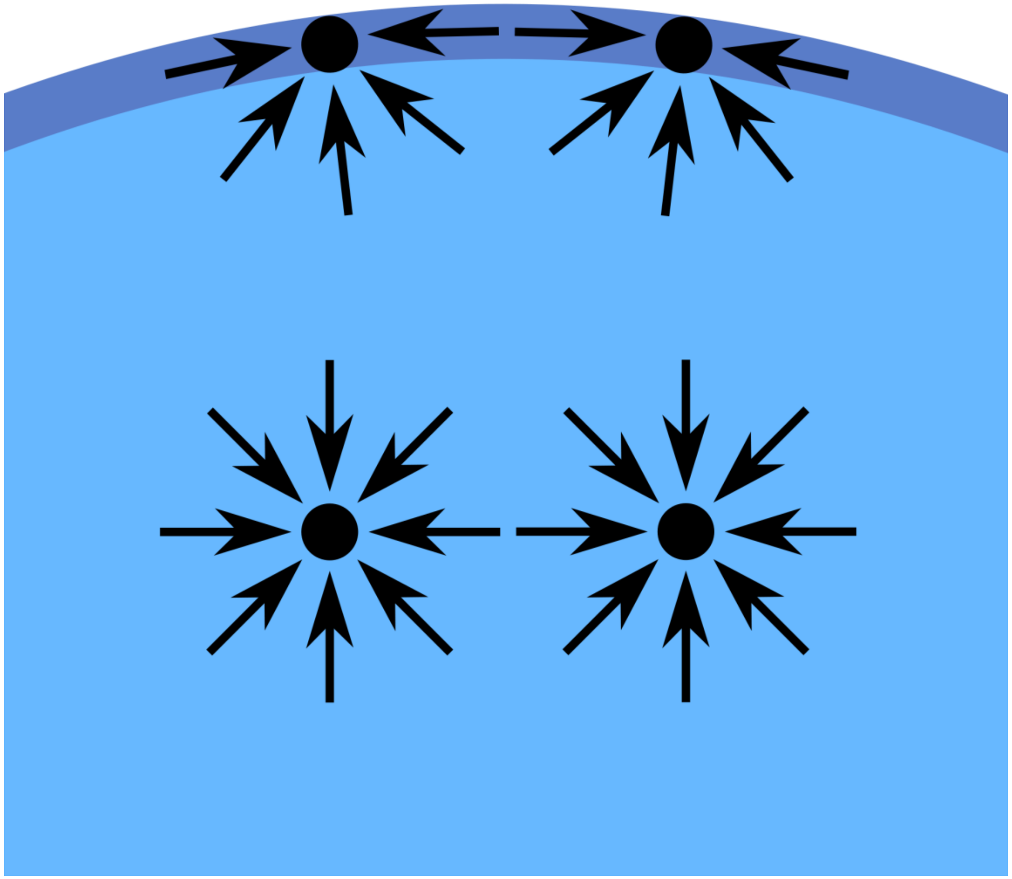
- why do some liquids "spread" on surfaces, others "bead up"
- why do paper towels, fabrics, sponges … soak up liquid?
- how do soaps and detergents "dissolve" oil in water?
- why can liquids be cooled below the freezing point (supercooled)?
- why can liquids be heated above the boiling point (superheated), then suddenly and dangerously flash into vapor
- how do boiling chips prevent superheating?

water droplets “beading”
on a surface

steel paper clip
“floating” on water

water bug
“walking” on water

Surface Tension



Unbalanced attractive
intermolecular forces
at the surface of a solid
or a liquid pull molecules
At the surface inward,
creating **surface tension**.

Surface tension acts
like a thin, stretched
elastic film, compressing
the interior molecules.

Surface Tension - Thermodynamic Definition

The surface work $\mathrm{d}w_\mathrm{s}$ required to increase the surface area of a system from σ to $\sigma + \mathrm{d}\sigma$ is

$$\boxed{\mathrm{d}w_\mathrm{s} = \gamma\,\mathrm{d}\sigma}$$

Breaking attractive intermolecular forces to form new surface area requires work to be done on a system, leading to positive surface work for increasing surface area.

First Law (including *p*-*V* and surface work)

$$\boxed{\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \gamma\,\mathrm{d}\sigma}$$

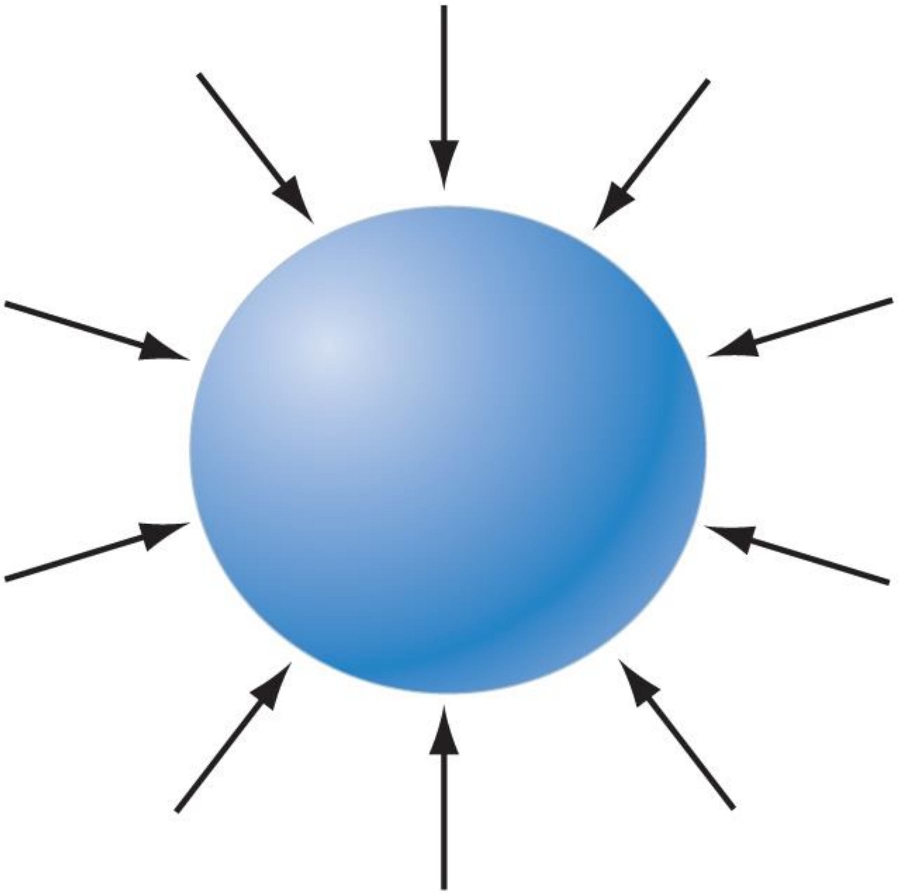
Surface Tension - Thermodynamic Definition

$\mathrm{d}G = \mathrm{d}(U - TS + pV)$ for the Gibbs energy gives

$$\boxed{\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \gamma\,\mathrm{d}\sigma}$$

The surface tension can be interpreted as the "Gibbs surface energy", the increase in G with surface area at fixed temperature and pressure.

$$\boxed{\gamma = \left(\frac{\partial G}{\partial \sigma}\right)_{T,p}}$$



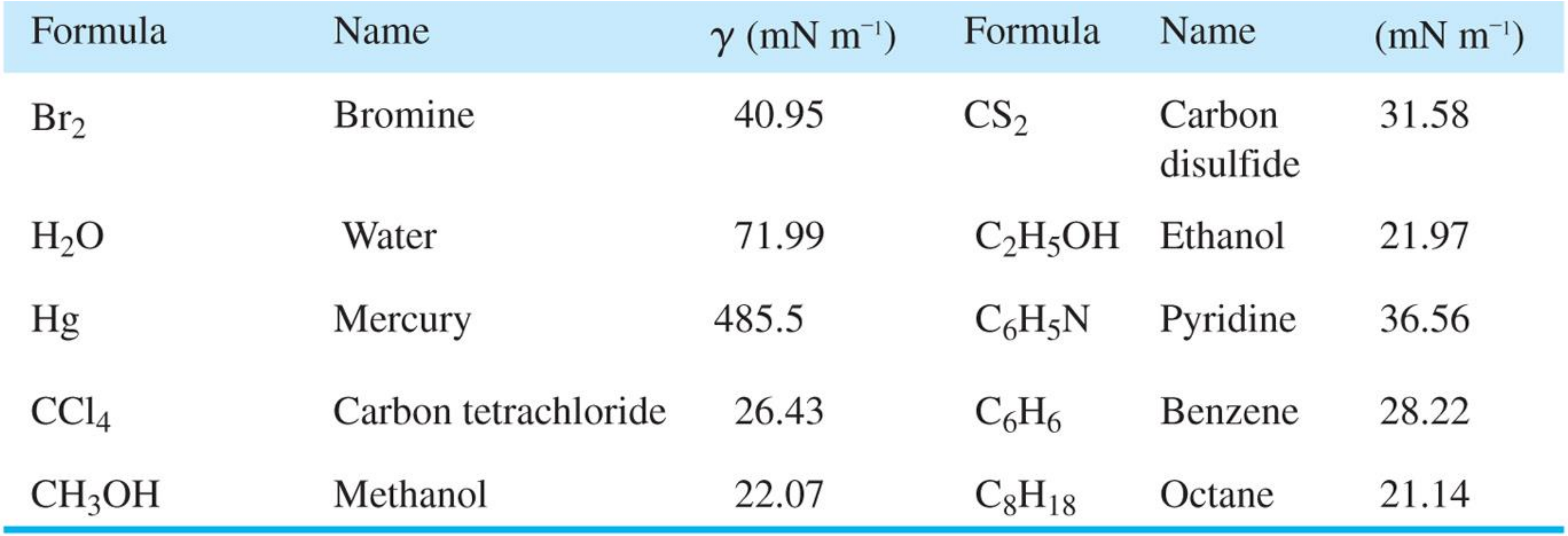
To minimize the Gibbs energy, a free droplet forms a sphere, the geometrical object with the smallest area per unit volume.

Applications?

Surface tension has units of **force per unit length**, such as N m^{-1}.

γ is analogous to a pressure (force per area) reduced by one dimension

Surface Tension of Selected Liquids at 25 ^oC



Formula	Name	γ (mN m^{-1})	Formula	Name	(mN m^{-1})
Br_2	Bromine	40.95	CS_2	Carbon disulfide	31.58
H_2O	Water	71.99	C_2H_5OH	Ethanol	21.97
Hg	Mercury	485.5	C_6H_5N	Pyridine	36.56
CCl_4	Carbon tetrachloride	26.43	C_6H_6	Benzene	28.22
CH_3OH	Methanol	22.07	C_8H_{18}	Octane	21.14

(Why are the surface tensions of water and mercury relatively high?)

Temperature Dependence of the Surface Tension

$$\gamma \approx \gamma_{\mathrm{o}} \left(1 - \frac{T}{T_{\mathrm{c}}} \right)^{n}$$

γ_{o} is a constant for each liquid

n is a constant (≈ 1.2 for non-hydrogen-bonded liquids)

What is the predicted surface tension at the critical temperature?

Is this value reasonable?

Example Calculate the work required to disperse 16 cm^3 of liquid water into a mist of 50-nm-diamter droplets at 20 $^{\circ}$C. Use $\gamma = 0.0728$ N m^{-1}.

$$w_{\text{s}} = \int_{\sigma_i}^{\sigma_f} \mathrm{d}w_{\text{s}} = \int_{\sigma_i}^{\sigma_f} \gamma\,\mathrm{d}\sigma = \gamma\int_{\sigma_i}^{\sigma_f} \mathrm{d}\sigma = \gamma(\sigma_f - \sigma_i)$$

σ_f = final surface area = number of droplets × area per droplet

$$= \frac{\text{total volume}}{\text{volume per drop}}\,4\pi r^2 = \frac{16 \times 10^{-6}\ \text{m}^3}{\frac{4}{3}\pi r^3}\,4\pi r^2 = \frac{3}{r}\,(16 \times 10^{-6}\ \text{m}^3)$$

$$= \frac{3\,(16 \times 10^{-6}\ \text{m}^3)}{25 \times 10^{-9}\ \text{m}} = 1920\ \text{m}^2$$

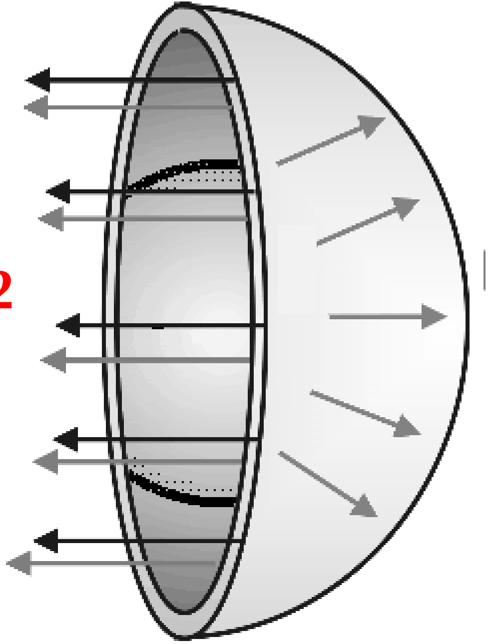
specific surface area
= (1920 m^2) / (16 g)
= **120 m^2 g^{-1}**

$$\sigma_i = \text{initial surface area} \approx 0 \qquad (\text{negligibly small, only a few cm}^2)$$

$$w_{\text{s}} = \gamma(\sigma_f - \sigma_i) \approx \gamma\,\sigma_f = (0.0728\ \text{N m}^{-1})\,(1920\ \text{m}^2) = \mathbf{140\ \ J}$$

Laplace Equation: The Pressure Inside a Curved Surface is Higher than the Outside Pressure

- **surface tension on circumference $2\pi r$ pulls left**
- **outside pressure on area πr^2 pushes left**
- **inside pressure on area πr^2 pushes right**

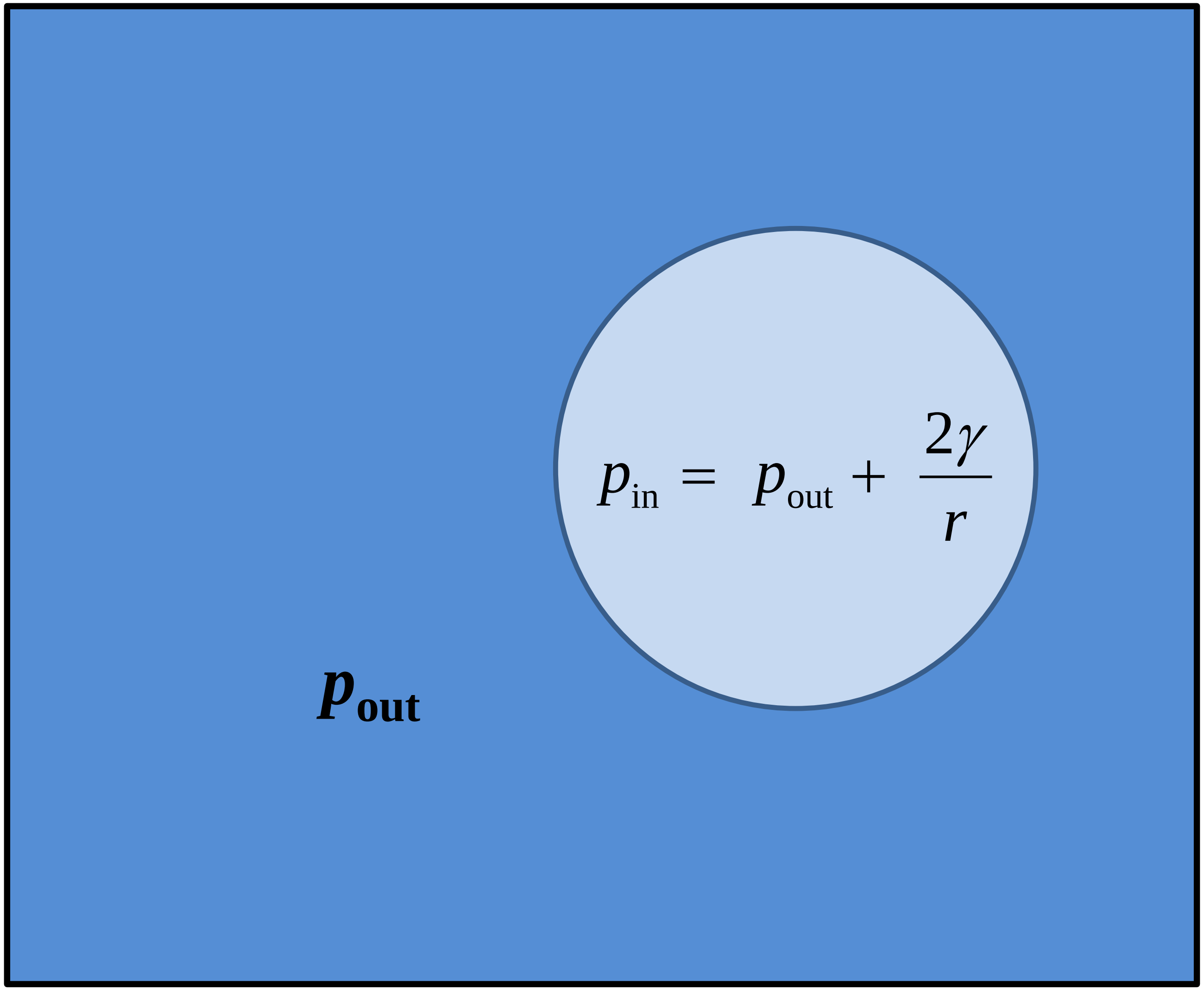


Horizontal Force Balance on a Bubble Cut in Half

$$\gamma 2\pi r + p_{out}\pi r^2 = p_{in}\pi r^2$$

$$\boxed{p_{in} = p_{out} + \frac{2\gamma}{r}}$$

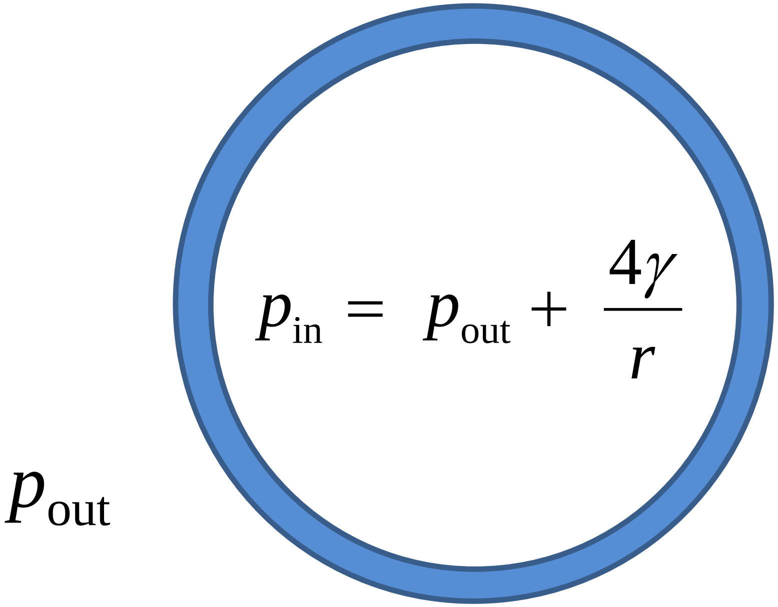
Pressure in a Bubble of Vapor in a Liquid



$$p_{\text{in}} = p_{\text{out}} + \frac{2\gamma}{r}$$

$\boldsymbol{p}_{\textbf{out}}$

Pressure in a Soap Bubble



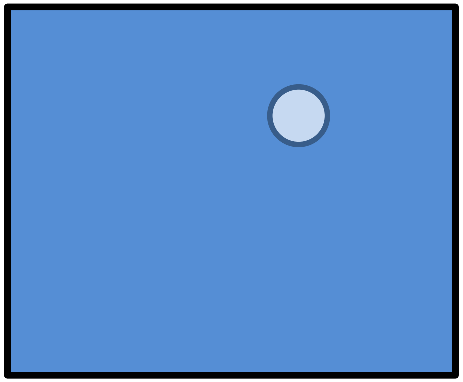
$$p_{\text{in}} = p_{\text{out}} + \frac{4\gamma}{r}$$

p_{out}

Why $\boldsymbol{p_{\text{out}} + 4\gamma/r}$ **?**

Pressure Inside a Bubble

Example Calculate the pressure inside a 50-nm diameter bubble of water vapor (steam) at the normal boiling point.



$T = 373.15\ \text{K}$ (100 °C)

$p_{\text{out}} = 101{,}325\ \text{Pa}$ (1 atm)

Data: surface tension $\gamma = 0.0589\ \text{N m}^{-1}$

$$p_{\text{in}} = p_{\text{out}} + \frac{2\gamma}{r}$$

$$= 101{,}325\ \text{Pa} + \frac{2\,(0.0589\ \text{N m}^{-1})}{25 \times 10^{-9}\ \text{m}}$$

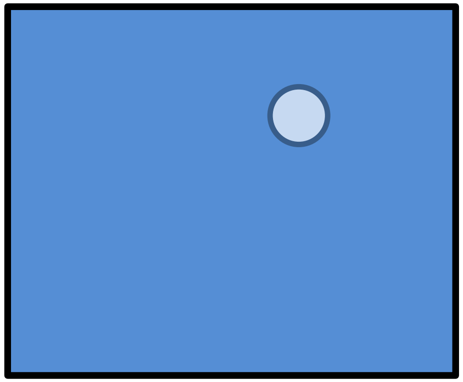
$$= 101{,}325\ \text{Pa} + 4{,}710{,}000\ \text{Pa}$$

$$\boxed{p_{\text{in}} = 4{,}810{,}000\ \text{Pa} \quad \textbf{(47.5 atm !)}}$$

**** The vapor in the bubble (*p* >> 1 atm) is <u>unstable</u> at 100 °C ****

Pressure Inside a Bubble - Superheating

A liquid heated in a clean, dust-free non-porous container can superheat and suddenly flash into vapor, with explosive violence.



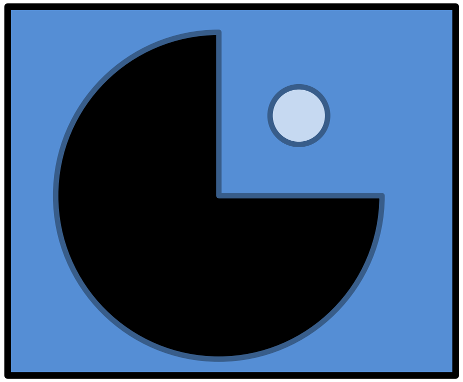
Why?

- the first bubbles of vapor are **microscopic in size** ($r \ll 1$ mm)
- surface tension pressure $2\gamma/r$ strongly compresses the vapor
- vapor in microscopic bubbles is unstable, reverts to liquid

(see calculations on the previous slide)

Pressure Inside a Bubble - Superheating

To prevent superheating and "bumping" use:



- boiling chips
- porous materials
- dust, dirt or sand …

These materials allow vapor to form on macroscopic surfaces with **macroscopic radii of curvature** and negligible vapor compression.

Supersaturation can be Lethal: Lake Nyos Disaster

Lake Nyos is a crater lake on an extinct volcano in Cameroon, Africa.

A magma chamber under the Lake supersaturates the deeper water with CO_2.

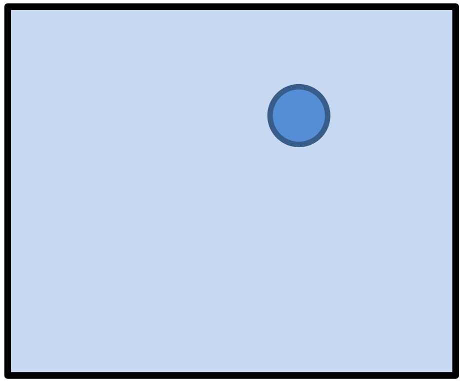
On the night of 21 August 1986, a small landslide into the Lake caused rapid mixing, bringing deep water to the surface.

Under reduced pressure, hundreds of thousands of tons of CO_2 gas were suddenly released from the supersaturated solution.

1,746 people and thousands of livestock were suffocated by the CO_2 gas (denser than air) flowing down valleys from the Lake.

Pressure Inside a Droplet - Supercooling

A vapor cooled in a clean, dust-free non-porous container can supercool below the condensation temperature.



Why?

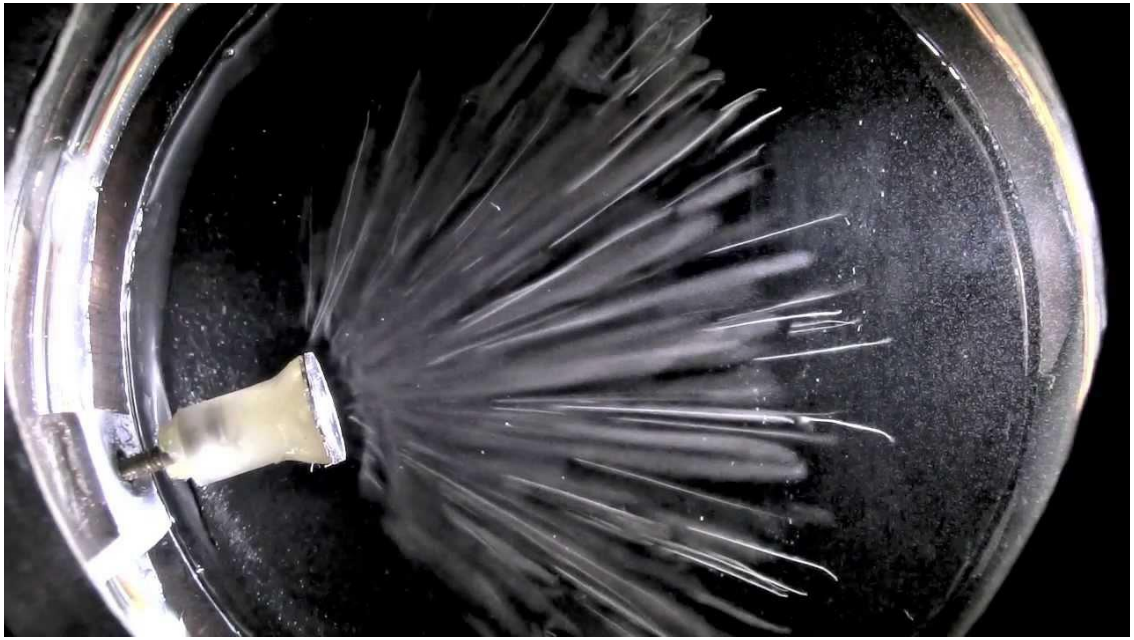
(application: "**cloud seeding**" to make it rain)

- the first droplets of liquid are **microscopic in size** ($r \ll 1$ mm)
- surface tension pressure $2\gamma/r$ strongly compresses the liquid
- the increased vapor pressure increases makes the droplets unstable

(see Section 8.7)

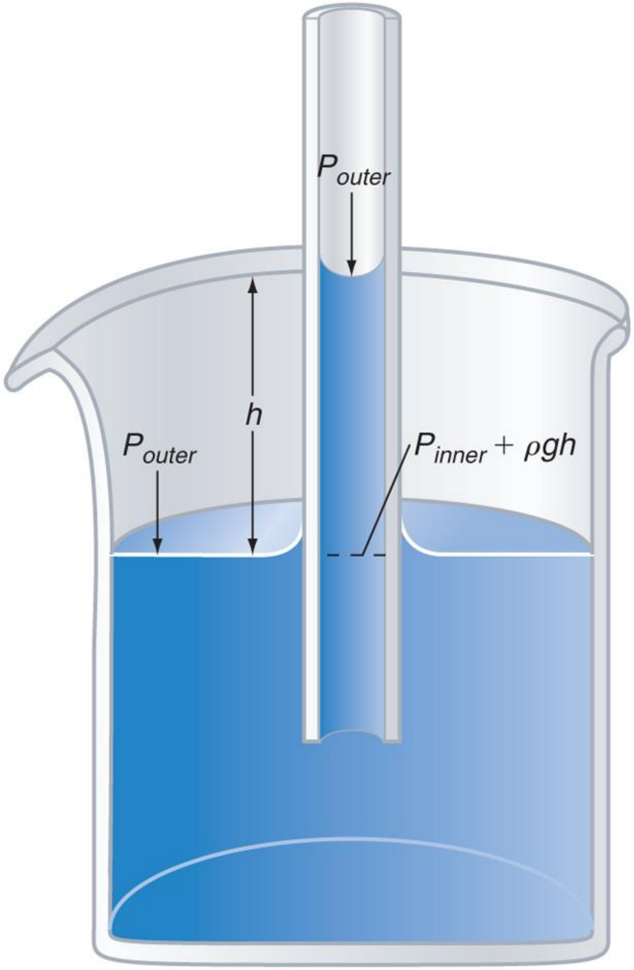
Pressure Inside a Droplet - Supercooling

Application: **Cloud Chambers**



- used to detect ionizing radiation (*e.g.*, alpha or beta particles)
- radiation passes through a supercooled vapor, such as ether
- ionized vapor molecules provide sites for condensation
- trail of condensed droplets indicates the particle tracks

Capillary Rise (also called Capillarity)



Dip a glass capillary tube
into liquid water.

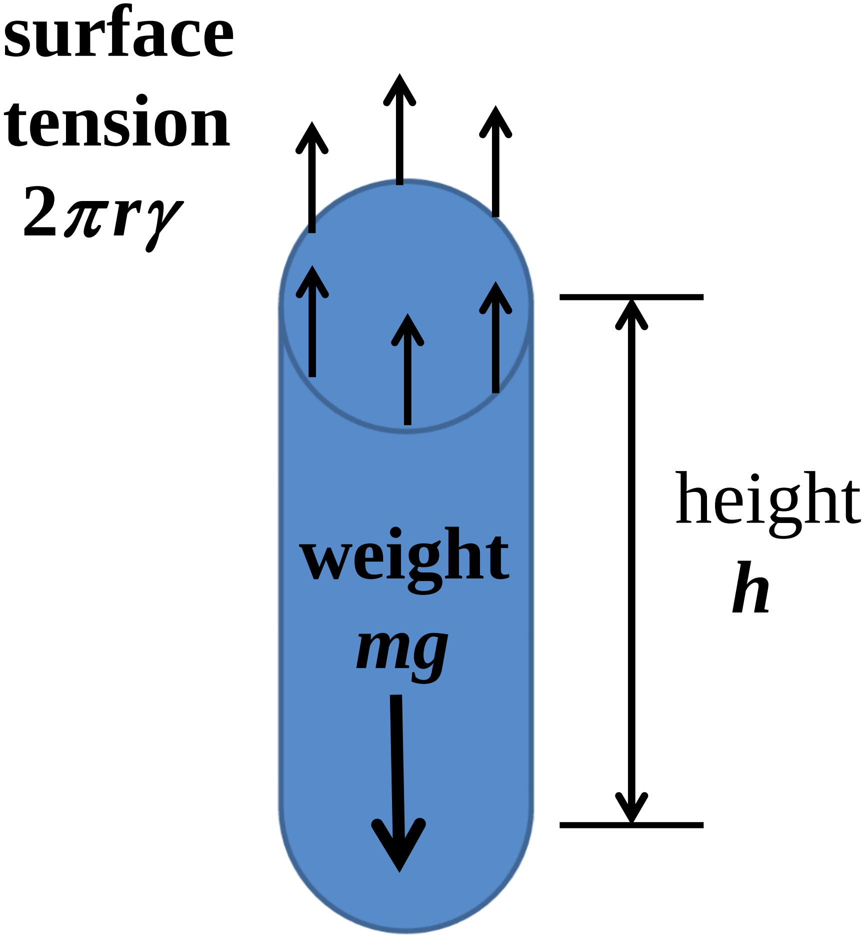
Water climbs up the tube.

Why?

<u>Applications</u>

- sap rises in trees
- candle wicks soak up wax
- pen tips soak up ink
- porous materials absorb liquid
- soil absorbs rainwater
- removing oil from porous rock can be expensive

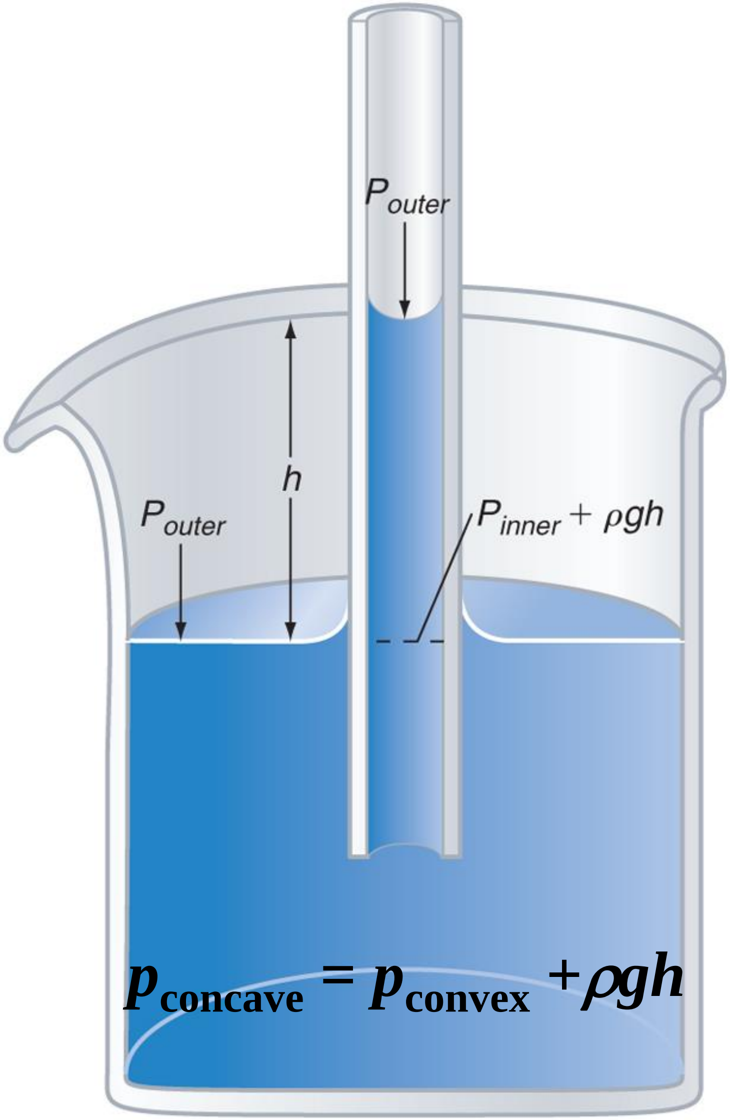
Capillary Rise (also called Capillarity)



surface tension
$2\pi r\gamma$

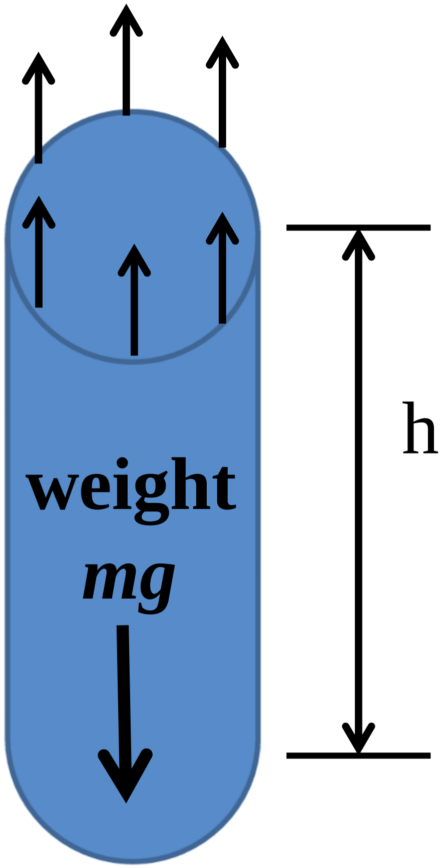
weight
mg

height
h



$$p_{\text{concave}} = p_{\text{convex}} + \rho gh$$

Capillary Rise (also called Capillarity)



surface tension
$\boldsymbol{2\pi r\gamma}$

weight
$\boldsymbol{mg}$

height
$\boldsymbol{h}$

Surface tension acting around the meniscus of circumference $2\pi r$ pulls a cylinder of liquid of height h and density ρ up the tube

$$mg = 2\pi r\gamma$$

$$V\rho g = 2\pi r\gamma$$

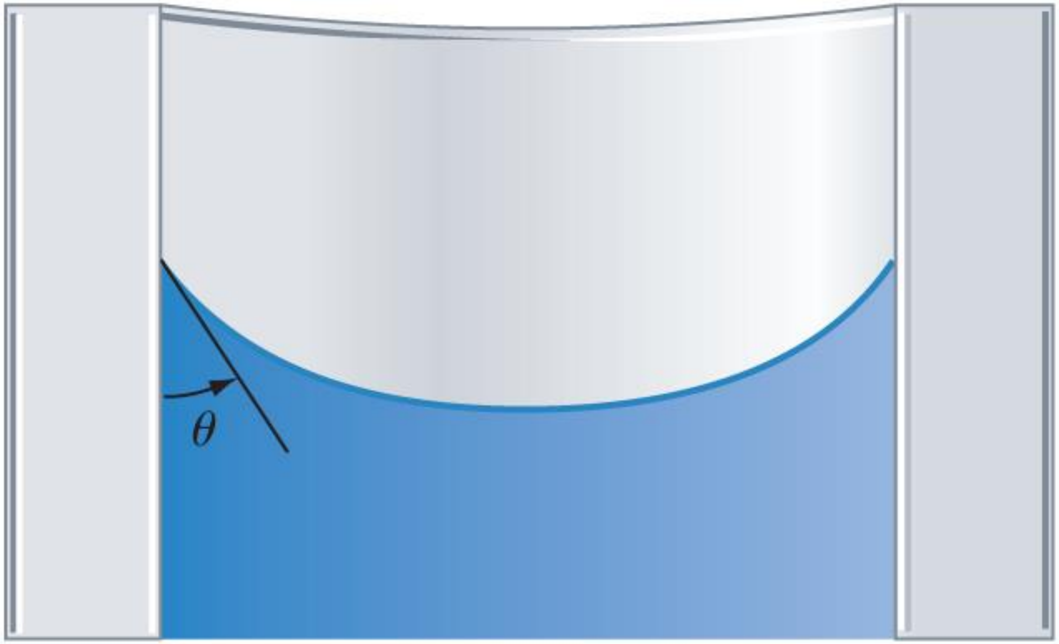
$$(\pi r^2 h)\rho g = 2\pi r\gamma$$

capillary rise

$$\boxed{h = \frac{2\gamma}{\rho g r}}$$

$$\begin{aligned} p_{\text{concave}} &= p_{\text{convex}} + \rho g h \\ &= p_{\text{convex}} + (2\gamma/r) \end{aligned}$$

Capillary Rise (also called Capillarity)



If the liquid doesn’t wet the tube material (**contact angle θ > 0°**) only the vertical component of the surface tension force pulls the liquid up the tube.

capillary rise

$$\boxed{h = \frac{2\gamma\cos\theta}{\rho\, g\, r}}$$

Capillary Rise (also called Capillarity)

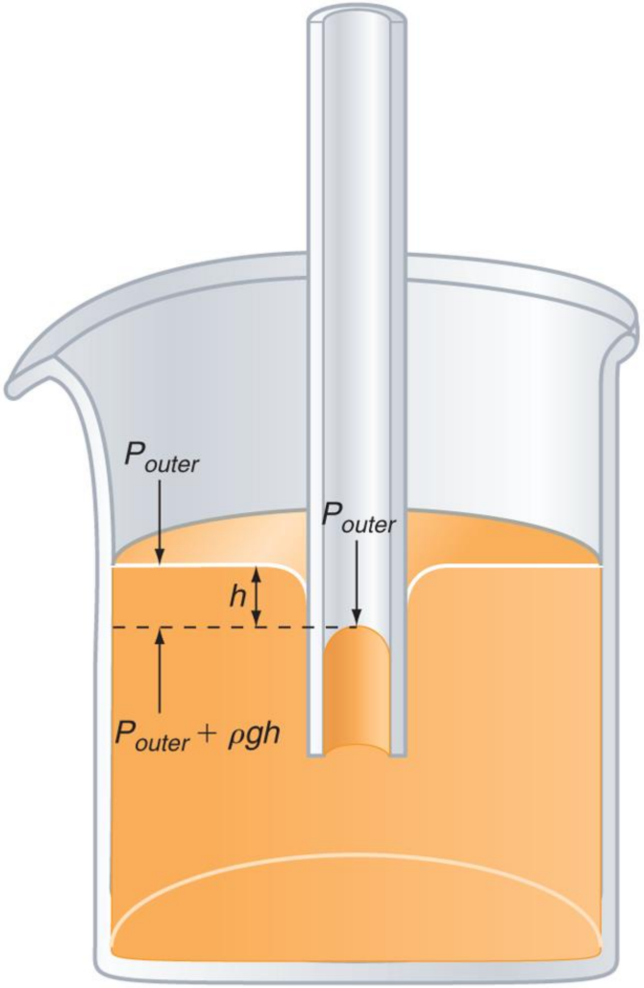
If the liquid is completely nonwetting (*e.g*, mercury on glass):

$$\theta = 180^{\circ}$$
$$\cos\theta = -1$$

surface tension pulls liquid
down the tube

capillary
depression
$(h < 0)$

$$\boxed{h = \frac{2\gamma\cos\theta}{\rho g r}}$$



Section 8.9 Chemistry in Supercritical Fluids

and

Section 8.10 Liquid Crystals

reading assignment